UNIVERSITY
OF MICHIGAN

MAR 18 1952

PHYSICS
LIBRARY

REGISTERED No. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XXXIV] *SECTION A* [No. 5

NOVEMBER, 1951

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

THE CHEMICAL BEHAVIOUR OF SULPHUR COMPOUNDS

Part III. Kinetics of the Gaseous Reaction Between Hydrogen Sulphide and Sulphur Dioxide*

By A. R. Vasudeva Murthy and B. Sanjiva Rao, F.A.Sc.

(Indian Institute of Science, Bangalore)

Received February 5, 1951

Introduction

The demonstration of the rapid reaction between hydrogen sulphide and sulphur dioxide in the presence of water was a common lecture-room experiment as early as 1812. Cluzel[1] noticed that no combination would result if the gases were first dried over calcium chloride. Many investigators[2] have studied the reaction in a more or less qualitative way, but their results throw little light on the nature of the gaseous reaction, because they permitted water to condense in the reaction system. The overall reaction is known to be

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S.$$

Lewis and Randall[3] studied the equilibrium in the reaction, at the temperature of boiling sulphur. Later, Randall and Bichowsky[4] investigated the equilibrium in this system at a temperature above 800° C. and noticed that at this temperature, hydrogen was present in small quantities, in the equilibrium mixture.

H. A. Taylor and W. A. Wesley[5] measured the velocity of the combination of hydrogen sulphide and sulphur dioxide in pyrex reaction tubes at temperatures ranging from 370° C. to 730° C. The velocity was found to be proportional to the surface area of the reaction chamber. This proved that the glass surface acted as a contact catalyst.

B. S. Rao[6] noticed that silver sulphide could act as an efficient catalyst for the union between the two gases, provided it was activated by a certain amount of moisture. To catalyse the union of the two gases at the surface of glass, a very much higher vapour pressure of water was found to be necessary than was the case with silver sulphide.

* Part of the Thesis submitted by A. R. Vasudeva Murthy for the M.Sc. Degree of the Mysore University.

The investigations described in this paper, constitute a study of the kinetics of the reaction between hydrogen sulphide and sulphur dioxide in an all-glass apparatus, wherein the vapour pressure of water was kept sufficiently low with the aid of an appropriate hygrostat, so that, while no detectable reaction took place at the surface of glass, there was adequate union at the silver sulphide. In order to maintain constant humidity at different levels, various hygrostats were used.

Experimental

In the study of the kinetics of this reaction, it was found essential to have a constant pressure of water vapour, and uniform composition of the gaseous mixture, throughout the system. These two conditions were secured by using a hygrostat and an all-glass, gas circulation pump.

Hygrostat.—The hygrostat consisted of a mixture of a crystal hydrate and its anhydrous salt or a lower hydrate. The following hygrostats[7] were used to obtain different vapour pressures of water, in the reacting system:—

	V.P. of water in mm. of Hg at 25 °C.
(1) Oxalic acid. $(COOH)_2.2H_2O \rightleftharpoons (COOH)_2 + 2H_2O$	.. 2·20
(2) Sodium bromide. $NaBr.2H_2O \rightleftharpoons NaBr + 2H_2O$	.. 5·47
(3) Barium bromide. $BaBr_2.2H_2O \quad BaBr_2 \cdot H_2O + H_2O$	.. 10·56
(4) Magnesium sulphate. $MgSO_4.7H_2O \rightleftharpoons MgSO_4.6H_2O + H_2O$	.. 12·46
(5) Sodium sulphate. $Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$	.. 19·15

Preparation of Hygrostats

(1) *Oxalic acid.*—Oxalic acid was dehydrated by the method recommended by Clarke and Davis[8] involving the use of boiling carbon tetrachloride for dehydration of the crystals. (*Cf.* Villiers[9a]; Rising and Stieglitz[9b].)

(2) *Sodium bromide.*—The anhydrous salt was obtained by heating the crystals for 24 hours at 110° C.[10]

(3) *Barium bromide.*—The monohydrate was obtained by heating the hydrate at 80° C. for 24 hours.

(4) *Magnesium sulphate.*—Magnesium sulphate hexahydrate was obtained by heating the heptahydrate for 24 hours at 40° C.

(5) *Sodium sulphate.*—Sodium sulphate decahydrate was heated in an oven at 110° C. for 24 hours.

The following catalysts were used in the present investigation:—

(1) Silver sulphide.

(2) Cobalt thiomolybdate.

(3) Cobalt sulphide.

(4) Molybdenum sulphide.

(1) *Silver sulphide.*—The silver sulphide was prepared by the reaction between silver oxide and sodium thiosulphate solution.

$$Ag_2O + Na_2S_2O_3 \longrightarrow Ag_2S + Na_2SO_4$$

500 ml. of 0·5 N sodium hydroxide was carefully added to 500 ml. of 0·5 N silver nitrate solution with constant stirring, in a 2 litre beaker and to the freshly precipitated silver oxide, 500 ml. of 0·5 N sodium thiosulphate was added gradually, when all the silver oxide was converted into silver sulphide. The solution was boiled for a few minutes. The precipitate was filtered and washed several times with distilled water, then with alcohol and dried at 100° C. for 24 hours. The sulphide was finely powdered in an agate mortar to pass through a sieve of 200 mesh, and kept in a well stoppered bottle.

(2) *Cobalt thiomolybdate.*—Through 20% solution of ammonium molybdate made alkaline with ammonia, hydrogen sulphide was passed for a long time. A red solution of ammonium thiomolybdate was obtained.[11] The solution was concentrated by slow evaporation when blood red crystals, appearing green in reflected light, were obtained.

These crystals were dissolved in distilled water and treated with a solution of 20% cobalt sulphate. The solution was chilled in a refrigerator, causing the precipitate to settle. The solution was filtered at the pump and the precipitate washed with distilled water several times, and finally with alcohol. The precipitate was dried at 110° C. for 24 hours. The dark mass obtained, was powdered to pass through a 200-mesh sieve.

(3) *Cobalt and Molybdenum sulphide.*—These sulphides were precipitated with hydrogen sulphide from their corresponding sulphates. The sulphides were powdered to pass through a 200-mesh sieve.

Hydrogen sulphide.—Hydrogen sulphide was prepared by the action of water on aluminium sulphide. The gas was frozen by liquid air, the impurities pumped off, and the solid allowed to evaporate. The gas was collected and stored in glass globes.

Sulphur dioxide.—Sulphur dioxide obtained from a cylinder of commercial liquid sulphur dioxide, was frozen by liquid air, the impurities pumped

off, and the solid allowed to evaporate. The gas was collected and stored in glass globes.

Construction of the Circulating Pump

Porter, Bardwell and Lind[12] designed an all-glass, double acting, electromagnetic pump. This was improved upon by Funnel and Hoover.[13] Though this improved type had greater capacity, it was found that its horizontal valve system was not satisfactory. Livingston[14] overcame this defect by replacing the horizontal valve system with a vertical valve system, thereby minimising the friction. He also added a third solenoid. The three solenoids acted in succession and controlled the vertical movement of the piston. When this pump was constructed in this laboratory and worked, the piston had a tendency to fall down and smash the whole apparatus. Furthermore, the entire system formed a single unit which could not be easily cleaned. In order to avoid these difficulties, three ground glass joints were introduced in the solenoid unit and four such joints in the valve system. A separate vertical valve unit was constructed, which could be easily removed for cleaning. These solenoids were introduced in the horizontal position. The middle one acted as a controlling field and kept the piston movements under check. Details of the set-up of the pump are given in Fig. 1.

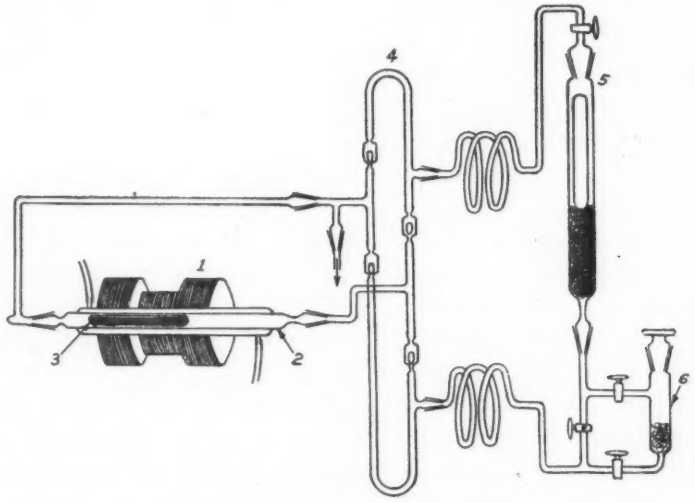


Fig. 1. All Glass Circulation Pump

1. Solenoids
2. Barrel
3. Piston
4. Valve System
5. Hygrostat Tower
6. Catalyst Chamber

The cylinder was 80 cm. long and had an internal diameter of 1 cm. The piston was 25 cm. long and fitted the barrel fairly snuggly. Enclosed in the piston were lengths of soft iron wire, embedded in paraffin. The valves consisted of very thin glass bulbs (about 4 mm. in diameter and about 0·5 gm. in weight). They were unground and rested in carefully made constrictions, in 5 mm. tubing. The valve system could be easily detached from the solenoid portion.

The solenoids were 7·5 cm. long and were separated by fibre disks. They were formed from 2,500 turns of enamelled copper wire on a brass tube which was also used as a water jacket. The tube was mounted on a wooden frame. The outer solenoids were excited alternately, 45 to 60 times per minute, by means of a rotating commutator, driven by an electric motor. The middle solenoid was continuously in action.

When adjusted to make 45 strokes a minute, this pump forced 20 litres of air per hour at atmospheric pressure against a head of 0·5 cm. of concentrated sulphuric acid. The pump circulated dry air in a closed system (containing a sulphuric acid bubbler) at all pressures down to 3 mm. of mercury. In order to overcome the heating in the solenoid and maintain the pump at room temperature, water was continuously passed through the jacket.

Construction of the Reaction Chamber

The outlet and the inlet of the circulating pump were connected by means of ground glass joints to the reaction vessel. The reaction vessel consisted of a tower, partially filled with the hygrostat, and a catalyst chamber as shown in Fig. 1.

Procedure

The circulation pump and the reaction vessel were thoroughly cleaned. The vessels were dried by rinsing with anhydrous methyl alcohol, followed by purified carbon tetrachloride. A current of hot air was employed to sweep off the carbon tetrachloride vapours. 10 g. of the hygrostat mixture was kept in the tower, over plugs of glass wool (that had been previously cleaned with acid, washed and dried). The catalyst chamber had 5 g. of the catalyst, supported over plugs of glass wool.

The reaction vessel along with the circulation pump, was evacuated for half an hour and tested for vacuum tightness. The catalyst chamber was then shut off. A measured quantity of sulphur dioxide (about 100 ml. at a pressure of 35 cm. of mercury) was let into the pump. The appropriate quantity of hydrogen sulphide was then allowed into the reaction vessel,

The mixture of the two gases was circulated in the hygrostat chamber for about 45 minutes to ensure that the mixture had acquired the vapour pressure of the hygrostat. The reaction mixture was then passed through the catalyst chamber.

The initial pressure reading was noted down, after bringing the level of mercury in the gas burette to the reference mark, so that the volume of the reacting gases was constant, when the pressure was read. The progress of the reaction was measured at frequent intervals by noting the fall in pressure. The pressures were read with the aid of a cathetometer.

Results

The rate of reaction between the hydrogen sulphide and the sulphur dioxide could be calculated from the pressure readings. The sulphur produced during the reaction was retained by the catalyst and the water evolved was taken up by the hygrostat. The volume of the system had been previously determined by allowing a known volume of dry air (100 ml.) at atmospheric pressure to expand into the evacuated reaction vessel. The volume of the reaction vessel could be varied, when necessary, by introducing sealed glass tubings into the hygrostat tower. In the present series of experiments, the volume of the vessel was adjusted to be about 400 ml.

The vapour pressure of water inside the system was constant, and was taken into account in computing the reduction in pressure due to the reaction between sulphur dioxide and hydrogen sulphide.

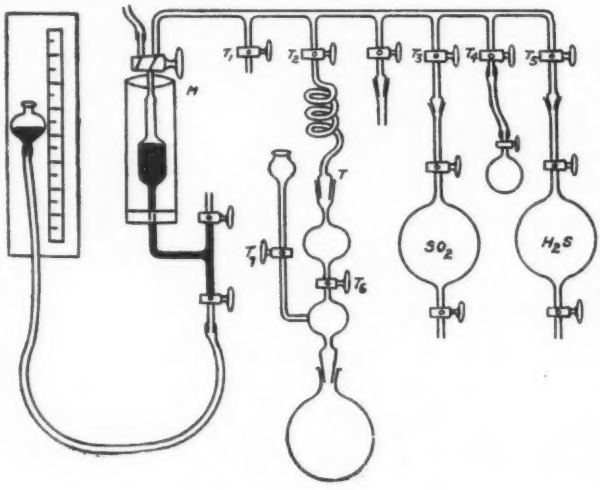


Fig. 2

After the reaction was over, the residual gas was pumped out and absorbed in 30% caustic soda solution using the arrangement shown in Fig. 2. To ensure complete absorption of the two gases by the alkali, dry hydrogen was let into the reaction chamber and conveyed to the absorption vessel. This procedure was repeated several times. The sulphide and sulphite of sodium produced in the absorption vessel were estimated by the method of Kurtenacker and Wollak.[15] These analytical values served as a check on the volumes of the residual gases as measured by the fall in pressure.

The order of the reaction could be determined by finding out the time required to undergo a definite fraction of the original concentration, employing the equation

$$\frac{T_2}{T_1} = \frac{C_1^{n-1}}{C_2},$$

where n was the order of the reaction. Time required to undergo half the reaction was calculated in a representative experiment. Invariably the ratio $\frac{T_2}{T_1}$ was found to be equal to $\frac{C_1}{C_2}$ so that n was always equal to 2. This indicated that the reaction was of the second order. Values of K calculated on the assumption that the reaction was (*a*) unimolecular and (*b*) termolecular were not constant and it was therefore clear that the reaction was bimolecular.

In the reaction:—

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S$$

for every ml. of sulphur dioxide consumed, 2 ml. of hydrogen sulphide would be utilised. The velocity of the reaction was therefore

$$-\frac{dx}{dt} = K(a - x)(b - 2x)$$

where a and b were the initial concentrations of sulphur dioxide and hydrogen sulphide respectively. The following equation obtained on integration:

$$K = \frac{2 \cdot 303}{t(2a - b)} \cdot \log \cdot \frac{(a - x)b}{(b - 2x)a}$$

could be used to calculate K, the velocity constant of the reaction. The total fall in the pressure would be $3x$. The results of various experiments are indicated in the following tables:—

EXPERIMENT NO. 1. *Silver Sulphide Catalyst*

V. pres. of barium bromide hygrostat = 10·56 mm. Temp. 25° C.
Initial partial pressure of SO_2 in cm. of Hg = $pSO_2 = 4·75$; $pH_2S = 7·18$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	11·93	..	..
5	10·49	1·44	3·18
10	9·28	2·55	3·15
15	8·48	3·45	3·12
20	7·68	4·25	3·11
25	6·98	4·95	3·26
35	6·23	5·70	3·13
45	5·33	6·60	3·13
60	4·88	7·45	3·15
75	3·83	8·10	3·19
90	3·38	8·85	3·17
180	1·73	10·20	3·12
240	1·73	..	..

* This is the pressure reading *less* partial pressure of moisture.

EXPERIMENT NO. 2. *Silver Sulphide Catalyst*

V. pres. of magnesium sulphate hygrostat = 12·46 mm. Temp. 25° C.
$pSO_2 = 4·1$, $pH_2S = 8·2$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	12·30	..	..
5	10·65	1·65	3·78
10	9·40	2·90	3·81
15	8·35	3·95	3·86
20	7·55	4·75	3·83
30	6·30	6·00	3·87
45	5·05	7·25	3·86
60	4·25	8·05	3·86
90	3·20	9·10	3·84
120	2·55	9·75	3·80
240	0·10	12·20	..

EXPERIMENT NO. 3. *Silver Sulphide Catalyst*

V. pres. of sodium sulphate hygrostat = 19·15 mm. Temp. 25° C.
$pSO_2 = 6·3$, $pH_2S = 6·3$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	12·6	..	..
5	10·35	2·25	4·61
10	8·85	3·75	4·62
15	7·70	4·90	4·57
20	6·90	5·70	4·50
30	5·70	6·90	4·57
45	4·65	7·95	4·51
60	4·10	8·50	4·52
90	3·55	9·05	4·57
120	3·50	9·10	..
240	3·50	9·10	..

EXPERIMENT NO. 4. *Cobalt Thiomolybdate Catalyst*

V. pres. of barium bromide hygrostat = 10·56 mm. Temp. 25° C.

$pSO_2 = 5·95$, $pH_2S = 5·95$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	11·90	..	..
5	9·80	2·10	5·98
10	7·85	4·05	5·84
15	6·65	5·25	5·93
20	5·90	6·00	5·85
30	4·85	7·05	5·91
45	4·44	7·90	5·84
60	3·55	8·35	5·87
90	3·10	8·80	..
120	3·10	8·80	..
240	3·10	8·80	..

EXPERIMENT NO. 5. *Cobalt Thiomolybdate Catalyst*

V. pres. of magnesium sulphate hygrostat = 12·46 mm. Temp. 25·8° C.

$pSO_2 = 4·3$, $pH_2S = 8·6$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	12·90	..	..
5	10·10	2·80	6·35
10	8·35	4·55	6·35
15	7·05	5·85	6·41
20	6·15	6·75	6·37
30	4·85	8·05	6·40
45	3·70	9·30	6·33
60	3·00	9·90	6·39
90	2·15	10·75	6·42
240	0·05	12·80	..

EXPERIMENT NO. 6. *Cobalt Thiomolybdate Catalyst*

V. pres. of sodium sulphate hygrostat = 19·15. Temp. = 26° C.

$pSO_2 = 4·40$, $pH_2S = 8·80$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	13·20	..	..
5	10·00	3·20	7·21
10	8·10	5·10	7·15
15	6·75	6·45	7·24
20	5·70	7·50	7·47
30	4·50	8·70	7·38
45	3·40	8·80	7·30
60	2·70	10·50	7·37
90	1·95	11·25	7·28
240	0·05	13·15	..

EXPERIMENT NO. 7. *Cobalt Sulphide Catalyst*

V. pres. of barium bromide hygrostat = 10·56 mm. Temp. = 25·3° C.
$pSO_2 = 5·80$, $pH_2S = 5·80$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	11·60	..	..
5	9·80	1·80	4·24
10	8·50	3·10	4·21
15	7·55	4·05	4·36
20	6·80	4·80	4·15
30	5·60	6·00	4·29
45	4·70	6·90	4·10
60	4·10	7·50	4·15
90	3·40	8·20	4·22
120	3·05	8·55	4·24
240	2·95	8·65	..

EXPERIMENT NO. 8. *Molybdenum Sulphide Catalyst*

V. pres. of barium bromide hygrostat = 10·56 mm. Temp. 25·7° C.
$pSO_2 = 4·20$, $pH_2S = 8·40$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	12·60	..	..
5	10·45	2·15	4·85
10	9·00	3·60	4·76
15	7·85	4·75	4·78
30	5·95	6·90	4·80
45	4·50	8·10	4·76
60	3·70	8·90	4·79
90	2·70	9·90	4·85
120	2·15	10·45	4·79
240	0·05	12·50	..

* This is the pressure reading less partial pressure of moisture.

It was found that when oxalic acid and sodium bromide hygrostats were used, there was no indication of any reaction in presence of the various catalysts.

In view of the catalytic effect of boron trifluoride and of aluminium chloride on certain chemical reactions, it was considered to be of interest, to find out if boron trifluoride or aluminium chloride would activate the silver sulphide.

The boron trifluoride was prepared by the method described by Booth and co-workers.[16] The vessel in which the reaction between hydrogen sulphide and sulphur dioxide in presence of boron trifluoride was tried, was a 100 ml. flask fitted with a ground glass joint and connected to the gas burette system (Fig. 2).

It was found that even after 24 hours there was no reaction at all. In another experiment silver sulphide was kept in the reaction flask and boron trifluoride let in. It was found that no reaction at all took place between the hydrogen sulphide and the sulphur dioxide. Boron trifluoride therefore did not activate the silver sulphide.

Experiments were carried out in a similar way to find out if anhydrous aluminium chloride would catalyse the reaction between hydrogen sulphide and sulphur dioxide. It was noticed that there was no detectable reaction between the two gases even after 24 hours. The chloride had thus no activating influence on silver sulphide.

SUMMARY OF THE RESULTS

	Catalyst	Hygrostat	V. pres. of hygrostat in mm. of Hg at 25° C.	$K \times 10^3$
1	Silver sulphide ..	Oxalic acid	2·20	No reaction
2	,, ..	Sodium bromide	5·47	,,
3	,, ..	Barium bromide	10·56	3·13
4	,, ..	Magnesium sulphate	12·46	3·82
5	,, ..	Sodium sulphate	19·15	4·52
6	Cobalt thiomolybdate ..	Oxalic acid	2·20	No reaction
7	,, ..	Sodium bromide	5·47	,,
8	,, ..	Barium bromide	10·56	5·80
9	,, ..	Magnesium sulphate	12·46	6·43
10	,, ..	Sodium sulphate	19·15	7·31
11	Cobalt sulphide ..	Barium bromide	10·56	4·21
12	Molybdenum sulphide ..	Barium bromide	10·56	4·83
13	Silver sulphide and Boron trifluoride	..	..	No reaction

DISCUSSION

The results show that certain metallic sulphides can catalyse the union between hydrogen sulphide and sulphur dioxide but the sulphides have always to be activated by moisture before they can function as catalysts. The vapour pressure of water in the oxalic acid or sodium bromide hygrostats is evidently insufficient to activate the silver sulphide or cobalt thiomolybdate. The vapour pressure of the barium bromide hygrostat, however, is adequate. The catalytic activity increases with a rise in the vapour pressure of water in the system, as can be gathered from the higher values of the velocity constant, in the magnesium sulphate hygrostat. The highest values for K are obtained in the sodium sulphate hygrostat.

Silver sulphide has the least catalytic activity. Cobalt sulphide and molybdenum sulphide are better and cobalt thiomolybdate is the best catalyst

of the four metallic sulphides tried. Cobalt thiomolybdate, it is of interest to note, is known to be a good catalyst for the oxidation of hydrogen sulphide.

The mechanism of the reaction between sulphur dioxide and hydrogen sulphide has been a subject of much controversy. Dalton[17] expected the production of polythionic acid along with water and sulphur. Thomson[18] regarded the reacting mixture as sulphite of hydrogen sulphide (SO_2, H_2S) Lang and Carson[19] stated that the union of the gases in terms of the equation $2H_2S + SO_2 \rightarrow 3S + 2H_2O$, was itself the primary reaction, in view of the fact, that even though water is absent, sulphur dioxide and hydrogen sulphide in liquid condition, slowly form sulphur. Klein[20] believed that a liquid surface was necessary to bring about the union between the two gases, but did not find any correlation between the dielectric constant of the liquid and its capacity to catalyse the reaction.

H. A. Taylor and W. A. Wesley[5] found that the rate of reaction, between hydrogen sulphide and sulphur dioxide at elevated temperature, was proportional to the surface area of the chamber, indicating the heterogeneity of the reaction. They suggested a mechanism in which it was assumed that each of the reactants was activated by adsorption on the surface of glass and that the reaction then took place only between the activated molecules. Further, they observed that the rate of reaction at constant temperature was directly proportional to pSO_2 and $p^{1.5}$ H_2S according to the equation

$$-\frac{dx}{dt} = K \times (p)^{1}_{SO_2} \times (p)^{1.5}_{H_2S}$$

It was thus suggested that the observed order of reaction was 2·5.

Various mechanisms have been suggested by different authors for the reaction between sulphur dioxide and hydrogen sulphide. Riesenfeld and G. W. Feld[21] have explained the formation of polythionic acids by assuming that sulphur dioxide and hydrogen sulphide react in solution producing sulphur monoxide as the primary product. Several investigators, however, have suggested that the primary product of the reaction between the two gases is thiosulphurous acid. B. S. Rao and M. R. A. Rao[22] who studied the reaction in non-aqueous solutions explained their observations on the basis of the formation of this acid. Deines and Grassman[23] in their study of the steps in the reaction between hydrogen sulphide and sulphurous acid also suggested that thiosulphurous acid was the primary product of the reaction. Thiosulphurous acid itself cannot be isolated because of its instability, but the methyl and the ethyl esters of the acid have been prepared by Meuwsen,[24] It is of interest to note that during their studies on the

splitting of ethylthiosulphite, Meuwsen and Gerhardt[25] isolated the ethyl ester of sulphoxylic acid. Sulphoxylic acid itself has not been isolated. Stamm and Wintzer[26] studied the hydrolysis of alkyl thiosulphites and explained the formation of certain products on the basis of the decomposition of thiosulphurous acid (the primary product of hydrolysis) into hydrogen sulphide and sulphurous acid. Stamm and Goehring[27] in explaining the mechanism of the formation of polythionic acid, by the interaction between hydrogen sulphide and sulphur dioxide in aqueous solution, postulate the formation of thiosulphurous acid as the primary product of the reaction and suggest its subsequent decomposition by hydrogen sulphide to yield sulphur.

$$H_2S + SO_2 \rightleftharpoons H_2S_2O_2$$

$$H_2S_2O_2 + H_2S \rightarrow 3S + 2H_2O.$$

Zil'berman[28] on the other hand explains the production of sulphur by the reaction between hydrogen sulphide and sulphur dioxide on the basis of the formation of dihydrogen sulphoxide as the primary product, the equations being:

$$2H_2S + H_2SO_3 \rightarrow 3HSOH \rightarrow 3H_2O + 3S.$$

The above mechanisms have been suggested for the reaction of hydrogen sulphide and sulphur dioxide in aqueous solution and should not be considered to be equally applicable to systems studied in the present investigation where the moisture was present only in traces.

It has already been stated that moisture has an "activating influence" on the silver sulphide catalyst and that in absence of adequate moisture, the reaction between hydrogen sulphide and sulphur dioxide does not take place at a detectable rate. The influence of water may be explained on the basis that the adsorbed moisture on the catalyst, owing to its avidity for sulphur dioxide, brings about a larger concentration of this reactant at the catalyst surface and thus promotes chemical union. With a view to confirm this, the adsorption of sulphur dioxide on the catalyst surface, was measured, using the McBain-Bakr Spring technique* to register the increase in weight of catalyst due to adsorption of sulphur dioxide, the moisture in the system being controlled by the use of different hygrostats. It was found that the adsorption of sulphur dioxide per gram of catalyst was always perceptibly higher in presence of moisture. A positive correlation between the quantity of sulphur dioxide adsorbed and the partial pressure of water in the system was also noticed.

* *cf. J. Am. Chem. Soc.*, 1926, **48**, 696.

The adsorption of hydrogen sulphide at the catalyst surface was also measured. It was found that the adsorption of this gas was much less. In this case also, moisture was found to increase adsorption but the influence of water was less pronounced.

The mechanism, the present authors suggest for the reaction between hydrogen sulphide and sulphur dioxide, is based on the formation of thiosulphurous acid as the primary product of the reaction. This reaction is reversible.† But under suitable conditions, the thiosulphurous acid, instead of reverting to sulphur dioxide and hydrogen sulphide can undergo decomposition on other lines. We suggest that decomposition can also take place in the following way:—

$$H_2S_2O_2 \rightarrow H_2SO + SO$$

and that the silver sulphide catalyses, the decomposition of dihydrogen sulphoxide as also the union between sulphur monoxide and hydrogen sulphide, the products formed being water and sulphur, in both these reactions.

Owing to its great reactivity, dihydrogen sulphoxide has not been isolated so far, but organic sulphoxides have been prepared.‡ Dihydrogen sulphoxide, it may be pointed out, is intermediate between hydrogen persulphide and hydrogen peroxide. It is well known that hydrogen peroxide is catalytically decomposed into water and oxygen by a variety of substances. The present authors have found that silver sulphide catalytically decomposes hydrogen persulphide vapour.§ Dihydrogen sulphoxide can be expected to decompose with at least equal ease, at the surface of silver sulphide, forming water and sulphur.

The sulphur monoxide formed along with dihydrogen sulphide reacts with hydrogen sulphide in presence of silver sulphide to yield water and sulphur, as already shown by B. S. Rao and M. R. A. Rao.[29]

The mechanism would therefore be

$$H_2S + SO_2 \rightarrow H_2S_2O_2$$
$$H_2S_2O_2 \rightarrow H_2SO + SO$$
$$H_2SO \xrightarrow{Ag_2S} H_2O + S$$
$$SO + H_2S \xrightarrow{Ag_2S} H_2O + S.$$

† *cf.* Noack, *Z. anorg. allgem. chem.*, 1925, **146**, 239; also Stamm and Goehring, *Naturwiss*, 1939, **27**, 317.

‡ *cf.* Fromm and Palma, *Ber.*, 1906, **39**, 3317.

§ Hydrogen persulphide vapour, obtained by the distillation under reduced pressure, of dry hydrogen persulphide, was passed over silver gauze previously coated with silver sulphide. There was marked increase in the weight of the gauze due to liberation of elemental sulphur.

Boron trifluoride and aluminium chloride did not catalyse the union between hydrogen sulphide and sulphur dioxide. Nor did the two substances have any activating effect on the silver sulphide. The inability of boron trifluoride and aluminium chloride to catalyse the reaction can perhaps be accounted for, by the fact that both of them form comparatively stable complexes[30] with hydrogen sulphide as well as sulphur dioxide. The formation of such complexes seems to prevent any chemical reaction between the two gases.

Summary

Certain sulphides, in presence of a small amount of moisture were found to catalyse the reaction between hydrogen sulphide and sulphur dioxide. The kinetics of this reaction was studied in a closed system, using an all-glass, gas circulation pump.

The partial pressure of water in the reacting system was maintained constant with the aid of a hygrostat [mixture of a hydrated salt and its anhydrous form (or lower hydrate)]. The higher the partial pressure of water, the greater was the velocity of reaction, for a given catalyst.

Of the sulphides employed, cobalt thiomolybdate was found to be the best catalyst. Cobalt sulphide and molybdenum sulphide were less efficient. Next in order of efficiency, was silver sulphide.

Boron trifluoride and anhydrous aluminium chloride were found to have no catalytic effect on the union between hydrogen sulphide and sulphur dioxide.

The mechanism of the reaction could be explained on the basis of the formation of thiosulphurous acid, as the primary product.

The authors wish to record their grateful thanks to Dr. K. Subba Rao and Dr. M. R. Aswathanarayana Rao, for their valuable help during the course of this work.

References

1. Cluzel .. *Ann. Chim. Phys.*, 1812, **84**, 162.
2. Mulder .. *Jahresb*, 1856, **86**.
   Corenwinder .. *Compt. rend.*, 1861, **53**, 140.
   Gripson .. *Ibid.*, 1863, **137**.
   Meyers .. *J. Prakt. Chem.*, 1869, **108**, 123.
   Antony and Magri .. *Gazzetta*, 1905, **35**, 206.
   Quam .. *J. Am. Chem. Soc.*, 1925, **47**, 103.
   Matthews .. *J. Chem. Soc.*, 1926, 2270.
3. Lewis and Randall .. *J. Am. Chem. Soc.*, 1918, **40**, 362.
4. Randall and Bichowsky .. *Ibid.*, 1918, **40**, 368.

5. Taylor and Wesley .. *J. Phy. Chem.*, 1927, **31**, 2165.
6. Sanjiva Rao, B. .. *Curr. Sci.*, 1943, **12**, 323.
7. ***International Critical Tables*** **3**, 209 (I Edition, 1928).
8. Clarke and Davis .. *Organic Synthesis*, 1922, **1**, 67.
9*a*. Villiers .. *Bull. Soc. Chem.*, 1880, (2) **33**, 415.
b. Rising and Stieglitz .. *J. Am. Chem. Soc.*, 1918, **40**, 726.
10. Thorpe .. *Dictionary of Applied Chemistry*, 1926, **6**, 194.
11. Newton Friend .. *Text Book of Inorganic Chemistry*, Part III, **8**.
12. Porter, Bardwell and Lind *Ind. Eng. Chem.*, 1926, **18**, 1086.
13. Funnel and Hoover .. *J. Phy. Chem.*, 1927, **31**, 1099.
14. Livingston .. *Ibid.*, 1929, **33**. 954.
15. Kurtenacker and Wollak .. *Z. Anorg. allgem. Chem.*, 1927, **161**, 201.
16. Booth and Willson .. *Inorganic Synthesis*, 1939, **1**, 21.
17. Dalton .. *A New System of Chemical Philosophy*, Manchester, 1808.
18. Thomson .. *Ann. Phil.*, 1818 (1) **12**, 441.
19. Lang and Carson .. *Proc. J. Chem. Soc.*, 1905, **21**, 158.
20. Klein .. *J. Phy. Chem.*, 1910, **15**, 1.
21. Riesenfeld and Feld .. *Z. anorg. allgem. chem.*, 1921, **70**, 119, 225.
22. Sanjiva Rao, B. and M. R. A. Rao *Nature*, 1931, **128**, 413.
23. Deines and Grassmann .. *Z. anorg. allgem. chem.*, 1934, **220**, 337.
24. Meuwsen .. *Ber.*, 1935, **68 B**, 121, 7.
25. ——— and Gerhardt .. *Ibid.*, 1935, **68 B**, 1011.
26. Stamm and Wintzer .. *Ibid.*, 1938, **71 B**, 2212.
27. ——— and Goehring .. *Naturwiss*, 1939, **27**, 317.
28. Zil'berman .. *J. Gen. Chem.* (*U.S.S.R.*), 1940, **10**, 1257.
29. Sanjiva Rao, B. and M. R. A. Rao .. *Curr. Sci.*, 1943, **323**, 12.
30*a*. Germann and Booth .. *J. Phy. Chem.*, 1926, **30**, 374.
b. Ruff .. *Ber.*, 1902, **35**, 4453.

A NOTE ON THE NATURE OF THE METAL-CARBON BOND IN ORGANO-ALKALI COMPOUNDS

By S. V. Anantakrishnan, F.A.Sc.

(Department of Chemistry, Madras Christian College, Tambaram)

Received September 6, 1951

Two contradictory statements in recent publications justifies a reconsideration of the problem in its various aspects. Sidgwick[11] remarks in his classification of these compounds "Colourless compounds like sodium methyl: *covalent* but highly associated", while Coates makes the observation.[2] "The alkyls of these elements include compounds with the properties of salts, *e.g.*, methyl potassium." The apparent abnormal behaviour of lithium methyl and the variations noticed in other cases further complicates the problem.

The spectroscopic work of Franck and Herzberg[4] has clearly shown that there can be very little homopolar interaction between the alkali and halogen atoms. One may reasonably extend this observation to other systems of similar electronic structures. Thus taking into account the electronic similarity in the series

$$F^-,\ OH^-,\ NH_2^-,\ CH_3^-\ BH_4^-$$

an ionic structure can be expected for the alkali salts. This is further strengthened by the work of Baughan, Evans and Polanyi[1] who find that the potential energy curves for ionic binding are strikingly lower than for covalent binding in sodium methyl.

A further piece of evidence is provided by considerations of electronegativity. Using Pauling's relation between electronegativity and ionic character of bonds[9] and the revised electronegativity values reported by Gordy,[5] the alkalimetal-carbon bond must have more than 50% ionic character with a minimum in the case of lithium compounds. The dipole moment measurements of Rogers and Young[10] has been reported to indicate covalency. There is reason, however, to suggest that electronegativity is by no means a reliable criterion for absolute indications of bond character. For instance, electronegativity suggests for the carbon-hydrogen bond only about 5% ionic character while the recent work of Coulson[3] has shown that this bond has about 40% ionic character. Qualitative comparisons can none the less be made. From electronegativity values, one gets for

the sodium chloride bonds about 65% ionic character and since each sodium ion is surrounded by six chloride ions, this gives an approximately 6% covalent character for each such bond. By analogy, the sodium-carbon bond should have only about 8% covalent character. The compounds can thus be reasonably considered to be salt-like rather than as associated covalent compounds.

Carrying the analogy further, it is of some interest to apply to the case of sodium methyl the Born-Haber cycle, as has been done in the case of sodium chloride and other alkali halides. One has further to assume that sodium methide has the same lattice structure as sodium chloride, with the methide ion taking the place of the halogen. The following sequence of changes may then be pictured:

I. The crystal sodium methyl is broken up into sodium and methyl ions. The energy absorbed in the process is the lattice energy U;

II. An electron is removed from the methide ion and added to sodium ion leaving sodium and methyl as '*monatomic*' gases. If the electron affinity of methyl is E and the ionisation potential of sodium is I then the energy involved in the change is E–I.

III. The alkali metal is condensed to the solid state and methyl '*atoms*' combine to form the dimer (ethane). If the sublimation energy of sodium is V and the dissociation energy of ethane 2X, the energy change in the two processes will be $-V-X$;

IV. The molecules of the reactants combine to reform the salt. The heat of reaction Q will be the heat evolved in the process.

Applying Hess's Law to the cyclic process, we get

$$U - Q = V + X - E + I$$

Of the various quantities involved, the sublimation energy and ionisation potentials of sodium are known experimentally, while Polanyi (*loc. cit.*) has calculated the electron affinity of methyl which can be used here. For the present purpose, no serious error arises by carrying the analogy of the electronic similarity of the series of anions to the parent molecules. The dissociation energy of ethane then gives us the value of energy of formation of methyl '*atoms*'. We are thus left with two unknown quantities, the lattice energy and the heat of formation of the compound. Taking the known qualitative correlation between ionic radii and lattice energy, the assumption can be made that the lattice energy of sodium methide has a value between that of sodium bromide and sodium iodide, probably near that of the bromide. The value of the heat of formation of the compound can be readily obtained.

Alternatively, the heat of formation may be computed. Since the potential energy curves of both covalent and ionic bond formation lies close to each other (Polanyi, *loc. cit.*) one can use for the energy of formation the calculated covalent bond energy. This can then give us the lattice energy. The results in both cases are given below in Table I.

TABLE I

Heat of formation of Na_2	17·5 K. Cals.	
Ionisation potential of Na	5·14 e. Volts	118 K. Cals.
Heat of sublimation of sodium ..	26 K. Cals.	
Heat of dissociation of ethane ..	88 K. Cals.	
Electron affinity of methyl	20 K. Cals.	

Lattice Energy — Heat of Formation $= 26 + 44 - 20 + 118 = 168$.

(1) Ionic radius methide ion .. 2·1 Å
„ of Br^- .. .. 1·96 Å
„ of I^- .. .. 2·20

Lattice energy of sodium bromide 174·6 (Landoldt and Born-
Lattice energy of sodium iodide 163·9 stein Tables)
Lattice energy of sodium methyl .. 170 K. Cals.
Heat of formation of sodium methyl −2·0 K. Cals.

(2) Using Pauling's geometric mean, covalent bond energy for Na — C bond is $(17{\cdot}5 \times 88)^{\frac{1}{2}} = 39$ K. Cals.
Lattice energy of sodium methide $= 168 + 39 = 207$ K. Cals.

It may be expected that the first one gives a more correct picture and the small value for the heat of formation is not surprising because of the analogy with the halides. Even the lattice energy obtained in the second case is below that of sodium fluoride and as such of the right order.

All these considerations indicate that for the alkyl derivatives of the alkali metals, the metal carbon bond is essentially an ionic bond and we shall attempt to interpret the properties, chemical and physical on this basis.

Among the physical properties that have been prominent in the study of these compounds may be mentioned the melting and boiling points, conductivity and solubility. We find on scrutiny that each one of these is quite consistent with an ionic type of binding even in the case of lithium compounds. While the external appearance and the relatively low volatility are adequate indications, low melting points of lithium ethyl and the higher alkyls have been presumed to indicate covalent binding and abnormal molecular weights in solution have been attributed to association of unknown nature. The ionic character of the bond between lithium and fluorine is

not in question and it will be of interest to compare these physical data for all the members of the first short period for both fluorides and the alkyl derivatives (Table II).

TABLE II

All the values have been taken from Sidgwick (*loc. cit.*). Boiling points are given within brackets. All temperatures are in °C.

Derivative	Li	Be	B	C	N	O	F
Fluoride ..	840 (1670)	840	(−101)	−184 (−128)	(−129)	(−144)	−223 (−187·9)
Methyl ..	High m.p.	200	(−20·2)	−19·5 (9·4)	(2·8)	(−23)	−141·8 (− 78·5)
Ethyl ..	90	ca 180 (200)	(95·0)	−31·1 (146·4)	(89·0)	(34·6)	−143·2 (− 37·7)

The sharp change from the first two members of the period to the others is noticeable *in all the cases* and even though the absolute value of the melting point of lithium ethyl is small, there is no justification for attributing this to covalency. There is a general tendency for melting points of ethyl derivatives to be lower than those of the corresponding methyl derivatives, only the gap is rather large in the case of lithium. It is not unlikely that this is due to the comparative small size of the cation with the anion of very much larger dimensions (radius ratio $< 0{\cdot}28$).

Turning to solubility, the evidence is again not unequivocal. While generally salts do not dissolve in typical organic solvents, there are instances of salts dissolving in benzene, *e.g.*, silver perchlorate. The small dipole moment of Lithium butyl observed by Rogers and Young (*loc. cit.*) in benzene has been taken as evidence of covalent character in these compounds. The formation of aggregates of ion pairs in a non-polar solvent can equally lead to small dipole moment values. In the absence of adequate data on dielectric absorption and measurements of dielectric loss it is not possible to test this but the six-fold association suggested by molecular weight determinations in benzene solution clearly indicates such cluster formation.

Conductivity in diethyl zinc is another uncertain evidence. Ethyl sodium and phenyl lithium conduct while phenyl sodium is a non-conductor in the same solvent.[6] In accounting for the small conductivity, however, it is not necessary to postulate the presence in solution of complexes formed by the covalent compound analogous to those that have been isolated in the solid state.[7] The work of Kraus and co-workers[8] in non-aqueous solvents

have clearly shown the considerable variations in the transport number of anion with solvent, the change affecting both cation and anion so that a small conductivity in a solvent of low dielectric constant does not necessarily mean that we are dealing with a covalent compound.

We may then conclude that none of the physical properties of the alkali alkyls are inconsistent with an ionic structure for the metal carbon bond. The chemical properties are not materially altered by this picture. The reactions of the metal alkyls are governed by the electrophilic activity of the metal cation and the proton affinity of the alkide ion and this is not altered whether one deals with the ions or with the polarised molecule in a covalent structure.

Summary

A consideration of the properties of the alkali alkyls shows clearly that the compounds are essentially salt-like in nature, the bond between the alkali ion and the alkide ions being ionic in character.

References

1. Baughan, Evans and Polanyi .. *Trans. Farad. Soc.*, 1941, **37**, 373.
2. Coates, G. E. .. *Quarterly Rev.*, 1950, **4**, 217.
3. Coulson, C. A. .. *Trans. Farad. Soc.*, 1942, **38**, 433.
4. Frank and Herzberg .. Quoted by (1).
5. Gordy, W. .. *Phys. Rev.*, 1947, **69**, 604.
6. A. von Grosse .. *Ber.*, 1926, **59**, 2653.
7. Hein, *et al.* .. *Z. Elektrochem.*, 1922, **25**, 469.
   .. *Z. Anorg. allgem. chem.*, 1926, **158**, 153.
8. Kraus, C. A. .. *Proc. N. Y. Acad. Sci.*, 1949, **51**, 789.
9. Pauling .. *Nature of the Chemical Bond* (Cornell, 1939), p. 70.
10. Rogers and Young .. *J.A.C.S.*, 1946, **68**, 2748.
11. Sidgwick .. *Chemical Elements and Their Compounds* (O.U.P., 1950), p. 81.

ANTHRAQUINONE AND ANTHRONE SERIES

Part VIII. 4-Halogenoalizarins and Their Derivatives

By B. S. Joshi, B. D. Tilak and K. Venkataraman, F.A.Sc.

(Department of Chemical Technology, University of Bombay)

Received September 15, 1951

Halogenation of α-hydroxyanthraquinone leads first to 4-halogeno- and then to 2:4-dihalogeno-1-hydroxyanthraquinones;[1] halogenation of β-hydroxyanthraquinone does not appear to have been studied. Direct chlorination or bromination of alizarin yields the 3-substituted halogeno derivatives, the directing group being the β-hydroxyl. When the β-hydroxyl group is methylated, the directing group is the α-hydroxyl and bromination gives 4-bromoalizarin-2-methyl ether.[2] Halogenated alizarins with the halogen atoms in the unsubstituted benzene ring of alizarin can be prepared synthetically by the condensation of halogenophthalic anhydrides with catechol.[3]

Chlorination of alizarin in aqueous suspension by sodium chlorate and hydrochloric acid,[4] or by passing chlorine through its solution in carbon disulphide in presence of iodine,[5] or by the action of iodine monochloride on alizarin[6] gives 3-chloroalizarin. When alizarin is heated with antimony pentachloride in a sealed tube at 100°, dichloro and tetrachloro derivatives of unknown constitution are obtained.[5] It has been stated that both 3-nitroalizarin and 4-nitroalizarin are "smoothly chlorinated" by sulphuryl chloride at 100°.[7] Chlorination of 3-methylalizarin with sulphuryl chloride in boiling nitrobenzene gives 4-chloro-3-methylalizarin.[8]

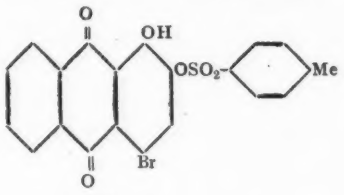
Bromination of hydroxyanthraquinones, such as alizarin, anthrapurpurin and flavopurpurin, is facilitated by reducing to the corresponding anthranol before treatment with bromine. Under these conditions bromine enters both the benzene rings and the *meso*carbon atoms; oxidation of the bromo derivative then gives a bromohydroxyanthraquinone.[9] Bromination of alizarin in carbon disulphide at 180°[10] or in boiling acetic acid in presence of sodium acetate,[11] leads to 3-bromoalizarin. Whereas bromination of alizarin with one mole of bromine in pyridine gives the 3-bromo derivative, two moles of bromine in the same solvent leads to 3-bromoalizarin pyridinium bromide.[12] Treatment of alizarin with excess of bromine and a little iodine in a sealed tube at 100° or 180° gives dibromo or tetrabromo

derivatives of unknown constitution,[5] while bromination in methanol at lower temperature yields 3:4-dibromoalizarin.[13]

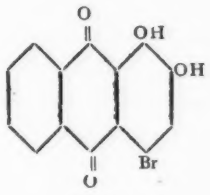
3-Iodoalizarin has been prepared by iodination of alizarin-1-methyl ether by means of iodine in warm pyridine and subsequent demethylation with hydrobromic acid in acetic acid.[14] It has also been synthesized from 3-nitroalizarin by methylation, reduction, replacement of the amino group by iodine, and final demethylation,[15] following the procedure employed earlier for the preparation of 4-iodoalizarin dimethyl ether.[16] This compound was prepared in the course of biological studies for which an alizarin derivative opaque to X-rays was required.[17]

4-Halogenoalizarins have not been reported so far, and their synthesis is now described. Although 4-bromoalizarin-2-methyl ether (IV) and 4-iodoalizarin dimethyl ether are known, their demethylation to 4-halogenoalizarins has not been reported.

4-Bromoalizarin (III) has now been prepared by bromination of alizarin-2-*p*-toluenesulphonate to give (II), followed by hydrolysis of the latter compound by sulphuric acid. The orientation of the bromine atom in (III) was proved by methylation to the known 4-bromoalizarin-2-methyl ether (IV).[11] Treatment of alizarin with *p*-toluenesulphonyl chloride in chloroform and pyridine at 28–30° gave alizarin-2-*p*-toluenesulphonate (I), but with excess of *p*-toluenesulphonyl chloride in pyridine at 100°, alizarin-1:2-di-*p*-toluenesulphonate was obtained.



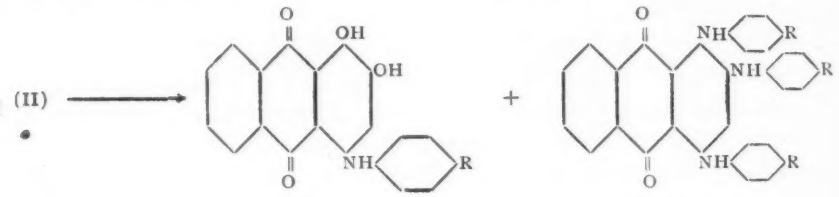
(II)



(III)

The bromine atom in (II) is reactive and by condensation with arylamines 4-arylaminoalizarins can be readily prepared. Thus, condensation of (II) with aniline in presence of anhydrous sodium acetate gave the alkali-soluble 4-anilinoalizarin (V; R = H), together with a deep blue-green alkali-insoluble product which has been shown to be 1:2:4-trianilinoanthraquinone (VI; R = H). When 4-halogeno- or 4-nitro-*o*-acylalizarins (see later) are condensed with arylamines and the products are treated with boiling hydrochloric acid to remove the excess of aniline, hydrolysis of the acyl groups takes place and 4-arylaminoalizarins are formed. 4-Anilino-

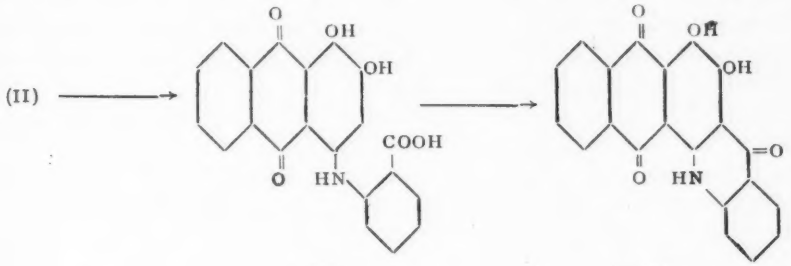
alizarin crystallized from hot toluene in shining violet plates, m.p. 263°, which were sparingly soluble in cold toluene. When the blue-green solution of the reaction product in toluene was chromatographed on alumina, a strongly adsorbed blue band and a green percolate were obtained. Removal of the solvent from the green percolate and crystallization from toluene and finally from acetic acid gave dark blue-green plates, m.p. 186°. The crystalline product was insoluble in hot aqueous sodium hydroxide and did not vat by the addition of sodium hydrosulphite. Elementary analysis and other properties indicated the constitution of the substance to be 1 : 2 : 4-trianilinoanthraquinone.[18] It has been noticed that 1 : 4-di-*p*-toluidinoanthraquinone is also non-vattable. Condensation of (II) with *p*-toluidine



gave the alkali-soluble 4-*p*-toluidinoalizarin (V; R= Me), violet plates, m.p. 228°, together with the alkali-insoluble 1 : 2 : 4-tri-*p*-toluidinoanthraquinone (VI; R= Me), shining dark blue plates, m.p. 220°.

Gonsalves, Kothare and Nadkarny have recently reported[19] the synthesis of 4-arylaminoalizarins by the interaction of arylamines with 4-nitroalizarin in presence of boric acid. They describe 4-anilinoalizarin as dark brown needles, m.p. 215°, and 4-*p*-toluidinoalizarin as brown needles, m.p. 204°. Since 4-anilino- and 4-*p*-toluidinoalizarins (V) prepared by us were different in melting point and other properties from the products described by Gonsalves, *et al.*, their reactions with 4-nitroalizarin were repeated. Pure 4-nitroalizarin (VIII), was prepared by nitration of alizarin dibenzoate to the 4-nitroderivative (VII), which was then hydrolysed with alkali. Condensation of (VII) or (VIII) with aniline, followed by treatment with boiling hydrochloric acid to remove the excess of aniline, gave the anilinoalizarin which was proved to be identical with 4-anilinoalizarin (V) prepared unambiguously from (II) as described earlier. Pure 3-nitroalizarin was also treated with aniline in presence of boric acid, but 3-anilinoalizarin was not formed, so that the " anilino-alizarin" of Gonsalves *et al.*, is not the 3-substituted derivative. Attempts to prepare 3-anilinoalizarin from 3-bromoalizarin likewise proved unsuccessful.

6:7-Dihydroxyanthraquinoneacridone (X), blue needles, m.p. 344–45°, was prepared by cyclization of 4-anilinoalizarin-2′-carboxylic acid (IX), prepared as usual from (II) and anthranilic acid. This acridone dyes cotton

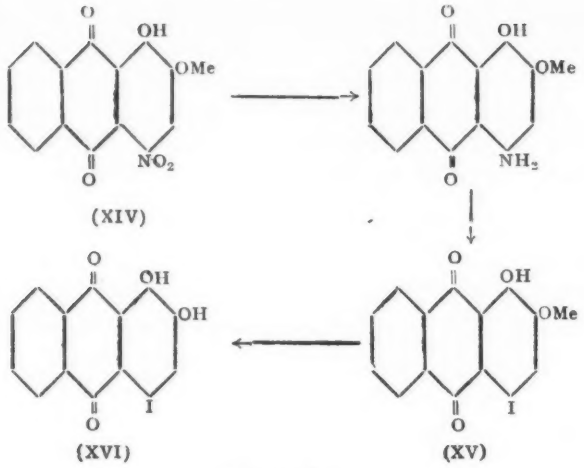


(IX) (X)

a blue-green shade which is not fast to soaping and changes to a blue-violet as a result of the presence of hydroxyl groups. In order to determine if the alkali sensitivity is primarily due to the β-hydroxyl group, the 2-methyl-ether (XI) of (IX) was prepared, but cyclization of (XI) with chlorosulphonic acid was accompanied by demethylation and the product was (X), instead of the expected 6-hydroxy-7-methoxyanthraquinoneacridone.

4-Chloro-2-*O*-*p*-toluenesulphonylalizarin (XII) was prepared by chlorination of (I) at 100° with sulphuryl chloride in nitrobenzene in presence of a little iodine. Hydrolysis of (XII) with sulphuric acid gave 4-chloroalizarin (XIII), orange plates, m.p. 239°. Reaction of (XII) with aniline gave 4-anilinoalizarin (V; R= H) and the alkali-insoluble blue-green 1:2:4-trianilinoanthraquinone (VI; R= H).

Iodination of (I) and alizarin di-*p*-toluenesulphonate by means of iodine monochloride in acetic acid and the iodination of alizarin-2-methyl ether and (I) by iodine in pyridine[14] were not feasible. Alizarin-2-methyl ether was nitrated to 4-nitroalizarin-2-methyl ether (XIV), m.p. 280°, the position of the nitro group being shown by the fact that demethylation with anhydrous aluminium chloride in nitrobenzene gave 4-nitroalizarin.[20] Condensation of (XIV) with aniline in presence of boric acid yielded 4-anilinoalizarin-2-methyl ether, obtained earlier from 4-bromoalizarin-2methyl-ether.[2] On reduction with yellow ammonium sulphide, (XIV) gave 4-aminoalizarin-2-methyl ether, from which by diazotization and treatment with aqueous potassium iodide 4-iodoalizarin-2-methyl ether (XV), crystallizing in red-orange needles, m.p. 235–37°, was prepared. Demethylation of (XV) by anhydrous aluminium chloride gave 4-iodoalizarin (XVI), m.p. 210°.



Experimental

4-*Bromo*-2-O-p-*toluenesulphonylalizarin* (*II*)

2-*O*-*p*-toluenesulphonylalizarin[21, 22] (4·0 g.), glacial acetic acid (80 c.c.), anhydrous sodium acetate (2·4 g.) and bromine (1·8 c.c.) were refluxed for one and a half hours and the solution filtered hot. Bright yellow needles (3·8 g.) separated on cooling, and the m.p. after crystallization from acetic acid was 180° (Found: Br, 16·8; S, 6·6. $C_{21}H_{13}BrO_6S$ requires Br, 16·9; S, 6·8%).

4-*Bromoalizarin* (*III*)

A solution of (II; 3·0 g.) in concentrated sulphuric acid (60 c.c.) was heated on a water-bath for one hour, and poured into ice-water. The orange precipitate (2·1 g.) obtained crystallized from acetic acid in bright orange plates, m.p. 230° (Found: C, 52·0; H, 2·3; Br, 24·8. $C_{14}H_7BrO_4$ requires C, 52·6; H, 2·2; Br, 25·0%). The substance gives violet solutions in aqueous sodium carbonate and sodium hydroxide, and a red solution in concentrated sulphuric acid.

4-*Bromoalizarin*-2-*methyl ether* (*IV*)

4-Bromoalizarin (90 mg.) was shaken with dimethyl sulphate (1 c.c.) in 10% sodium hydroxide (10 c.c.). The solution was kept alkaline by adding sodium hydroxide solution and warmed, when it turned yellow. It was cooled again and 10% caustic soda and dimethyl sulphate added. The process was repeated till the product gave a red precipitate in aqueous alkali,

The yellow solid which separated on acidification crystallized from acetic acid in lustrous orange needles, m.p. 236–37°; undepressed by adding the product of the bromination of alizarin-2-methyl ether.

4-Bromoalizarin (0·3 g.) and acetic anhydride (4 c.c.) were refluxed for 30 minutes and the mixture poured in ice-water. The *diacetate* (0·35 g.) crystallized from acetic acid in long lemon-yellow needles, m.p. 174–75° (Found: C, 54·1; H, 2·8; Br, 19·6. $C_{18}H_{11}BrO_6$ requires C, 53·6; H, 2·7; Br, 19·8%).

Alizarin di-p-*toluenesulphonate*

Alizarin (0·9 g.), *p*-toluenesulphonyl chloride (3·1 g.) and dry pyridine (9 c.c.) were shaken at room temperature for 15 minutes when yellow flakes appeared. The mixture was heated on the water-bath for four hours and the solution kept overnight. The pale yellow product which separated was filtered, washed with methylated spirit (10 c.c.) and crystallized from acetic acid; the light yellow plates melted at 187–88° (Found: C, 61·0; H, 3·7; S, 11·9. $C_{28}H_{20}O_8S_2$ requires C, 61·3; H, 3·6; S, 11·7%). The substance is insoluble in boiling 10% sodium hydroxide solution; in concentrated sulphuric acid it gives a red-brown solution from which a yellow precipitate separates on dilution. Hydrolysis of the di-*p*-toluenesulphonate (0·27 g.) with sulphuric acid (2·7 c.c.) at 100° for 15 minutes gave alizarin (0·12 g.).

4-*Anilinoalizarin* (*V*; *R* = *H*)

Aniline (24 c.c.) and anhydrous sodium acetate (2·0 g.) were heated to 150°, then cooled to 130° and (II; 4·73 g.) was added and the mixture heated to 190° for four hours. The resulting blue mass was poured into dilute hydrochloric acid, boiled and the blue product collected (3·0 g.). It was treated with cold toluene (300 c.c.) and filtered. The violet toluene-insoluble residue (0·3 g.) was crystallized four times from hot toluene, when 4-anilinoalizarin was obtained as shining violet plates, m.p. 263° (Found: C, 72·8; H, 3·7; N, 4·1. $C_{20}H_{13}NO_4$ requires C, 72·4; H, 3·9; N, 4·2%). The substance forms a violet solution in aqueous sodium hydroxide; the violet solution in sulphuric acid changes to a red-violet on the addition of boric acid. 4-Anilinoalizarin dyes chromemordanted wool a dull violet shade.

The extract obtained by treatment of the reaction mixture with toluene in the cold was chromatographed on alumina. A blue band was found to be strongly adsorbed and a green percolate was collected. After removal of the solvent from the percolate, the residue was crystallized from toluene and finally from acetic acid when it was obtained as shining dark blue-green plates, m.p. 186° (Found: N, 8·6. $C_{32}H_{23}N_3O_2$ requires N, 8·7%). The

product is insoluble in boiling 10% sodium hydroxide and does not vat with alkaline sodium hydrosulphite solution. It dissolves in concentrated sulphuric acid giving a honey-yellow solution which gradually changes to an eosin-red solution. Elementary analysis and other properties suggest that the alkali-insoluble product is 1 : 2 : 4-trianilinoanthraquinone.

4-p-*Toluidinoalizarin* (*V*; *R* = *Me*)

A mixture of (II; 2·6 g.), *p*-toluidine (10 g.) and anhydrous sodium acetate (2 g.) was heated at 190° for two hours. The blue solution was poured into water and steam-distilled to remove the unreacted *p*-toluidine. The resinous blue product (2 g.) was treated with cold toluene (400 c.c.) and filtered. The residue (0·35 g.) after two crystallizations from boiling toluene gave 4-*p*-toluidinoalizarin as violet plates, m.p. 228° (Found: N, 4·1. $C_{21}H_{15}NO_4$ requires N, 4·1%).

The blue solution, obtained by extraction with cold toluene, was chromatographed on alumina. It gave two major fractions: (1) a blue-violet fraction which was strongly adsorbed and (2) a fraction which gave a greenish blue percolate. Concentration of the percolate and two crystallizations of the product from benzene gave dark blue plates with a metallic lustre, m.p. 220° (Found: C, 80·3; H, 5·5; N, 7·7. $C_{35}H_{29}N_3O_2$ requires C, 79·6; H, 5·9; N, 8·0%). The product is insoluble in boiling caustic soda solution and does not vat by addition of sodium hydrosulphite. Elementary analysis and its properties suggest that it is 1 : 2 : 4-tri-*p*-toluidinoanthraquinone.

O-*Dibenzoyl*-4-*nitroalizarin*[23] (*VII*)

Finely powdered *O*-dibenzoylalizarin[12] (3 g.) was slowly added under stirring to a mixture of 77% nitric acid (5·5 c.c.) and concentrated sulphuric acid (8 c.c.) keeping the temperature below 5°. A pasty mass was obtained after half an hour, and after two hours the pale orange solid was added to crushed ice. The precipitate (2·4 g.) was crystallized twice from glacial acetic acid and once from ethyl alcohol, when the nitro derivative was obtained as clusters of yellow needles.

4-*Nitroalizarin* (*VIII*)

Hydrolysis of (VII) with 10% sodium hydroxide in boiling water-bath gave 4-nitroalizarin as shining orange yellow needles, m.p. 289° (dec.) (Found: N, 5·3. Calc. for $C_{14}H_7NO_6$; N, 4·9%).

4-*Anilinoalizarin from* 4-*nitroalizarin*

Dibenzoyl-4-nitroalizarin (VII; 0·5 g.), boric acid (0·4 g.) and aniline (5 c.c.) were heated in an oil-bath at 120° for 9 hours. The mixture was

poured into dilute hydrochloric acid, boiled, and the dark precipitate (0·65 g.) dissolved in cold toluene (40 c.c.) and filtered. The violet residue (0·36 g.) was crystallized thrice from boiling toluene; the violet plates of 4-anilinoalizarin had m.p. 263°, undepressed when mixed with the anilinoalizarin obtained from (II). The properties of the products obtained by the two methods were also identical.

4-Nitroalizarin (VIII) on similar condensation with aniline also gave 4-anilinoalizarin, m.p. 263°.

4-Anilinoalizarin-2′-carboxylic acid (*IX*)

4-*Bromo*-2-*O*-*p*-*toluenesulphonylalizarin* (1·58 g.), anthranilic acid (1 g.) anhydrous sodium acetate (0·2 g.), potassium carbonate (0·5 g.), copper bronze (0·3 g.) and amyl alcohol (30 c.c.) were heated in an oil-bath at 150° for 20 hours. The reaction mixture was filtered, washed with methanol, and the residue (1·4 g.) was extracted with aqueous ammonia. The purple solution was acidified with hydrochloric acid and the product was purified by precipitation from 10% sodium carbonate solution. The blue-violet anthranilinoalizarin had m.p. 268° (Found: N, 3·7. $C_{21}H_{13}NO_6$ requires N, 3·7%).

6:7-*Dihydroxyanthraquinoneacridone* (*X*)

4-Anilinoalizarin-2′-carboxylic acid (0·2 g.) was dissolved in concentrated sulphuric acid (8 c.c.) and the violet solution heated on a water-bath for 30 minutes. On pouring into ice-water, the blue precipitate (0·18 g.) was collected. Two crystallizations from *o*-dichlorobenzene gave long blue violet needles, m. p. 344–45° (Found: N, 4·4. $C_{21}H_{11}NO_5$ requires N, 3·9%). The acridone dyes a blue-violet shade from an olive green vat. The shade is not fast to soaping and considerable bleeding takes place. The shade is sensitive to acid, the shade obtained after dyeing and oxidation changing to blue-violet on souring.

N-1′-(3′-*Methoxy*-4′-*hydroxy*)*anthraquinonylanthranilic acid* (*XI*)

4-Bromoalizarin-2-methyl ether (1·2 g.), anthranilic acid (1 g.) anhydrous potassium acetate (0·8 g.), copper bronze (20 mg.) and amyl alcohol (20 c.c.) were heated at 150° for 24 hours. The mixture was filtered hot, washed with alcohol and the residue boiled for 30 minutes with dilute hydrochloric acid. It was filtered and washed with 10% sodium carbonate solution (20 c.c.). The residue, after washing with water, crystallized from glacial acetic acid in violet needles, m.p. 319–20° (Found: N, 3·8. $C_{22}H_{15}NO_6$ requires N, 3·6%).

6:7-*Dihydroxyanthraquinoneacridone* (*X*)

(*a*) The above acid (XI; 0·2 g.) was finely powdered and added to sulphuric acid (5 c.c.), and the violet solution heated on a water-bath for 30 minutes. Part of the product was sulphonated under these conditions and dissolved in water; the water-insoluble portion was the uncyclized acid.

(*b*) The acid (XI; 0·5 g.) was dissolved in chlorosulphonic acid (5 c.c.). After leaving for two days in a stoppered bottle, the resulting green solution was poured into crushed ice and the product collected (0·42 g.). It crystallized from *o*-dichlorobenzene in long blue-violet needles, m.p. 344–45°, undepressed when mixed with the 6:7-dihydroxyanthraquinoneacridone described above.

4-*Chloro*-2-O-p-*toluenesulphonylalizarin* (*XII*)

2-*O*-*p*-toluenesulphonylalizarin (5 g.), nitrobenzene (10 c.c.), sulphuryl chloride (5 c.c.) and a trace of iodine were heated on a water-bath for two hours. Nitrobenzene was removed by steam distillation, and the residue (5·9 g.) after two crystallizations from glacial acetic acid was obtained as yellow needles, m.p. 167° (Found: C, 58·4; H, 3·4; Cl, 8·2; S, 7·5. $C_{21}H_{13}ClO_6S$ requires C, 58·9; H, 3·0; Cl, 8·3; S, 7·5%).

4-Chloro-2-*O*-*p*-toluenesulphonylalizarin (XII; 1 g.) was condensed with aniline (5 c.c.), as in the case of (II) in presence of fused sodium acetate. The reaction mixture was treated with hydrochloric acid and dissolved in cold toluene. Two crystallizations of the residue from toluene gave blue-violet plates, m.p. 263°. The mixed m.p. of this product with 4-anilinoalizarin was undepressed. The toluene-soluble portion after chromatographic separation gave 1:2:4-trianilinoanthraquinone, m.p. 186° (Found: C, 79·1; H, 4·8; N, 8·6. $C_{32}H_{23}N_3O_2$ requires C, 79·8; H, 4·8; N, 8·7%).

4-*Chloroalizarin* (*XIII*)

The toluenesulphonyl derivative (XII; 1·5 g.) was heated on water-bath with concentrated sulphuric acid (30 c.c.) for one hour and the solution poured into ice. The product (1 g.) crystallized from acetic acid (60 c.c.) in orange plates, m.p. 239° (Found: C, 60·8; H, 3·0; Cl, 12·7. $C_{14}H_7ClO_4$ requires C, 61·2; H, 2·6; Cl, 12·7%).

4-Chloroalizarin (0·2 g.), acetic anhydride (2·5 c.c.) and anhydrous sodium acetate (0·1 g.) were refluxed for one hour and the yellow solution poured into crushed ice. The yellow *diacetate* crystallized from acetic acid in bright yellow plates, m.p. 168° (Found: C, 59·9; H, 2·9; Cl, 9·7. $C_{18}H_{11}ClO_6$ requires C, 60·3; H, 3·1; Cl, 9·9%).

4-Nitroalizarin-2-methyl ether (*XIV*)

Alizarin-2-methyl ether (1·0 g) was added to concentrated nitric acid (10 c.c.) at 28–30°. A red-brown solution was obtained from which yellow plates separated. It was poured into ice-water, and the yellow residue collected and crystallized twice from acetic acid. The shining yellow plates melted at 280° (Found: N, 4·7. $C_{15}H_9NO_6$ requires N, 4·7%).

4-Nitroalizarin

4-Nitroalizarin-2-methyl ether (0·5 g.) was dissolved in nitrobenzene (9 c.c.) at 150° and anhydrous aluminium chloride (0·7 g.) was added, when the yellow-orange solution changed to a purple red. After 30 minutes, it was poured into dilute hydrochloric acid, steam distilled, and the solid crystallized twice from acetic acid, when orange-yellow needles, m.p. 289° (dec.), were obtained. Mixed with 4-nitroalizarin (VIII), the melting point was not depressed.

4-Aminoalizarin-2-methyl ether

4-Nitroalizarin-2-methyl ether (1 g.) was refluxed with yellow ammonium sulphide (40 c.c.) for one hour, when a red-brown precipitate was obtained. It was collected, washed with hot water, dried (0·8 g.) and crystallized from aqueous pyridine. The dark red needles did not melt below 400° (Found: N, 5·0. $C_{15}H_{11}NO_4$ requires N, 5·2%). With concentrated sulphuric acid a yellow-red solution with an orange fluorescence is obtained; on addition of boric acid it changes to a bluish red solution with a strong yellow fluorescence.

4-Iodoalizarin-2-methyl ether (*XV*)

4-Aminoalizarin-2-methyl ether (0·5 g.) was dissolved in boiling acetic acid (15 c.c.) and hydrochloric acid (8 c.c.) added. On cooling, brown yellow needles of the hydrochloride separated. After addition of sodium nitrite solution (0·25 g. in 5 c.c. water) at 0°, and keeping for about 30 minutes the clear solution was poured into 10% aqueous potassium iodide (50 c.c.) and heated on water-bath for one hour. The brown precipitate was collected, washed and dried (0·62 g.). It crystallized from acetic acid in red-orange needles, m.p. 236–37° (Found: C, 47·6; H, 2·4; I, 33·1. $C_{15}H_9IO_4$ requires C, 47·4; H, 2·4; I, 33·4%).

4-Iodoalizarin (*XVI*)

The 2-methyl ether (XV; 0·1 g.) was dissolved in nitrobenzene (3 c.c.) at 120° and anhydrous aluminium chloride (0·1 g.) added. The brown

solution changed to violet. After 45 minutes, the solution was poured in dilute hydrochloric acid, steam-distilled to remove the nitrobenzene, and the dark-red residue (0·095 g.) collected. It crystallized from acetic acid in red-orange needles, m.p. 210° (Found: C, 46·0; H, 1·8; I, 34·4. $C_{14}H_7IO_4$ requires C, 45·9; H, 1·9; I, 34·7%). It dissolves in aqueous sodium carbonate and caustic soda giving violet solutions.

4-Anilinoalizarin-2-methyl ether

4-Nitroalizarin-2-methyl ether (XIV; 0·3 g.), boric acid (0·3 g.) and aniline (3 c.c.) were heated in a oil-bath at 120° for 8 hours. The solution was poured into hydrochloric acid, and the violet residue dissolved in cold benzene (100 c.c.) and filtered. The residue crystallized from hexane in violet plates, m.p. 198° (Found: N, 4·2. $C_{21}H_{15}NO_4$ requires N, 4·1%). The blue-violet solution in concentrated sulphuric acid changes to a fuchsine red on the addition of boric acid.

Summary

The synthesis of 4-chloro-, bromo- and iodo- alizarins is described. Bromination of 2-*O*-*p*-toluene sulphonylalizarin (I) in glacial acetic acid gave a monobromo derivative (II), which on hydrolysis yielded a new bromoalizarin (III). Methylation of (III) gave the known 4-bromoalizarin-2-methyl ether, showing that (III) is 4-bromoalizarin. Chlorination of (I) with sulphuryl chloride in nitrobenzene gave 4-chloro-2-*O*-*p*-toluenesulphonylalizarin (XII), which on hydrolysis yielded 4-chloroalizarin. Condensation of (II) and (XII) with aniline and *p*-toluidine led to 4-anilino- and 4-*p*-toluidinoalizarins. In addition to the 4-arylaminoalizarins, 1 : 2 : 4-trianilino and 1 : 2 : 4-tri-*p*-toluidinoanthraquinones were isolated by chromatography. Condensation of 4-nitroalizarin with aniline in presence of boric acid gave 4-anilinoalizarin, which was different from the product described by Gonsalves, *et al.*, as 4-anilinoalizarin. 6 : 7-Dihydroxyanthraquinoneacridone was prepared from (II) in the usual manner and examined as a vat dye. 4-Iodoalizarin-2-methyl ether (XV) was prepared from alizarin-2-methyl ether by nitration, reduction, and replacement of the amino group by iodine *via* the diazonium salt. Demethylation of (XV) with aluminium chloride gave 4-iodoalizarin.

Acknowledgment

Our thanks are due to the Council of Scientific and Industrial Research for the award of a Fellowship to one of us (B. S. J.), and to Mr. T. S. Gore for the microanalyses recorded in the paper.

REFERENCES

1. Ullmann and Conzetti .. *Ber.*, 1920, **53**, 826; Ullmann, D.R.P. 282, 494.
2. .. D.R.P., 158, 257.
3. Waldmann .. *J. prakt. Chem.*, 1938, **150**, 99.
4. Wedekind .. D.R.P., 189, 937.
5. Diehl .. *Ber.*, 1878, **11**, 187.
6. Gandbhir, *et al.* .. *Curr. Sci.*, 1950, **19**, 380.
7. .. B.P., 120, 528 (cited from Ref. 12).
8. Mitter and Biswas .. *Ber.*, 1932, **65**, 622.
9. .. D.R.P., 117, 923.
10. Perkin .. *J. Chem. Soc.*, 1874, 401.
11. —— and Haddock .. *Ibid.*, 1933, 1512.
12. Barnett and Cook .. *Ibid.*, 1922, 1376.
13. Dimroth, Schultze and Heinze .. *Ber.*, 1921, **54**, 3035.
14. Perkin and Story .. *J. Chem. Soc.*, 1931, 2620.
15. Pratt and Archer .. *J. Am. Chem. Soc.*, 1949, **71**, 2938.
16. Seer and Karl .. *Monatsh*, 1913, **34**, 631.
17. Epstein *et al.* .. *J. Am. Roentgenol*, 1946, **56**, 202.
18. .. *Cf.* D.R.P., 151, 511 (1:2:4-trianilinoanthraquinone from purpurin)
19. .. *J. Indian Chem. Soc.*, 1950, **27**, 479.
20. .. *Cf.* D.R.P., 150,322.
21. Perkin and Storey .. *J. Chem. Soc.*, 1928, 241.
22. Sen .. *J. Indian Chem. Soc.*, 1946, **23**, 383.
23. .. *Cf.* D.R.P., 66, 811.

ON THE SOLUBILITY OF RARE EARTH HYDROXIDES IN AQUEOUS SODIUM POTASSIUM TARTRATE

By G. S. Deshmukh, D.Sc.

(*Asst. Professor of Chemistry, Benares Hindu University*)

AND

K. V. Nayak, M.Sc.

Received May 1, 1951

[Communicated by Prof. S. S. Joshi, D.Sc. (Lond.), F.R.I.C., F.A.Sc.]

The nature of the complex rare earth tartrates and their dissolution in tartaric acid, alkalies and alkali tartrates have recently been studied by Britton and co-workers.[1,2] The precipitation of rare earths by NaOH is inhibited completely in the presence of tartaric acid; KOH and ammonia, however, precipitate only the yttrium earths under certain conditions.[3,4] These results show the property possessed by weak hydroxy acids of holding numerous metal bases (including rare earths) in solution at a high pH value where they should normally be precipitated. The difference in the basicity of rare earths should correspond to a difference in the solubility of their hydroxides in tartaric acid or/and aqueous alkali tartrates (Rochelle salt solution). No quantitative data are, however, available in the literature on the solubility behaviour of rare earth hydroxides towards sodium potassium tartrate solution. This information has now been obtained in respect of La, Ce^{iii}, Ce^{iv}, Er and Y hydroxides towards variously concentrated Rochelle salt solution.

Experimental

Merck's extra pure samples of oxides of lanthanum, cerium, yttrium and erbium were used to prepare the corresponding nitrate *hexa* (or *penta*) hydrate. A weighed quantity of the oxide was digested with pure nitric acid. The solution was evaporated on a steam-bath; the process of extraction of the syrupy residue with water and its evaporation was repeated till the solution was practically free from nitric acid. To an aliquot quantity (20 ml.) of the made up solution 25 ml. of NH_4OH (750 ml. of liquor ammonia of sp. gr. 0·885 diluted with 3 litres of water) was added followed by 100 ml. of Rochelle salt solution of a given concentration varied from 1 to 30%. The solution was boiled for one minute and filtered. The amount of rare earth oxide in the original nitrate solution was such that some hydroxide remained

undissolved after treatment with Rochelle salt solution. The quantity measured was the weight of oxide in the filtrate. This was done by igniting the precipitated oxalate and also by titrating its sulphuric acid solution against standard potassium permanganate. These results are expressed graphically in Fig. 1.

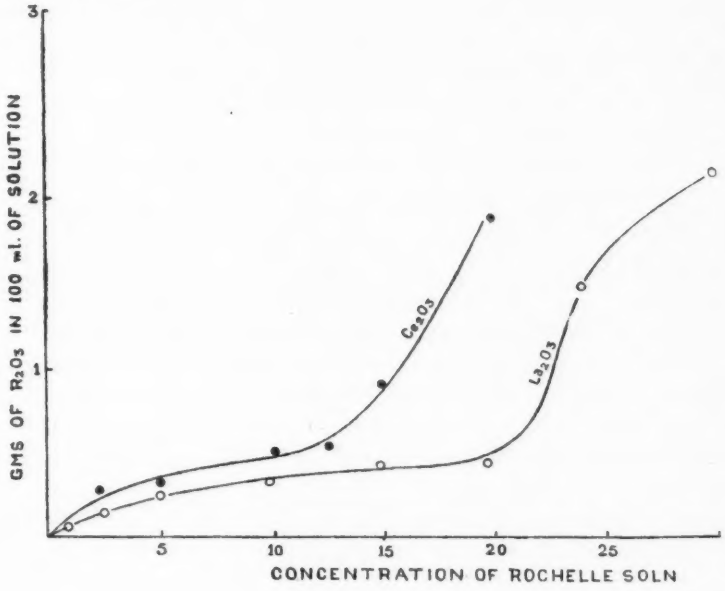


FIG. 1

It is seen (Fig. 1) that the solubility of lanthanum and cerous hydroxides first increases; reaches almost a constant value and finally rises abruptly, as the concentration of sodium potassium tartrate solution is raised progressively. It is, however, interesting that under identical experimental conditions ceric, yttrium and erbium hydroxides are not perceptibly soluble even when the strength of Rochelle salt solution is varied from 1 to 20%. That the rare earth tartrates dissolve readily in excess of tartaric acid or alkali tartrates is known.[1] The solvent action of the latter seems, therefore, to be analogous to that of weak hydroxy acid. The basicity of a solute should be an important determinant of its dissolution in an acid or its salt solution. The basic character of the rare earths, determined by their precipitation from salt solutions by ammonia, varies in the order $La > Ca^{iii} > Pr > Nd > Gd > Sm > Y > Tb > Ho > Er > Tm > Yb > Sc > Ce^{iv}$.[5] This should also be the order of decreasing solubility of their hydroxides in a

given solvent. It is, however, seen (Fig. 1) that cerous hydroxide is much more soluble than that of lanthanum. This, as also the negligibly small solubility of the corresponding ceric, erbium and yttrium compounds even in 20% Rochelle salt solution suggests that the dissolution in alkali tartrates, of the rare earth hydroxides is not determined by their basicities. Tartaric acid and its salts are strong peptizing agents.[6] The possibility whether this peptizing action was the cause of the marked dissolution of the above rare earth hydroxides was next investigated. It was ruled out from a failure to observe any coagulation or cataphoretic effect.

The sharp inflexions in the curves (*cf.* Fig. 1) indicative of the enhanced solubility of the La and Ce^{iii} hydroxides occur at a limiting concentration of the solvent corresponding to about 20 and 12·5% respectively; furthermore this critical concentration increases with the decreasing solubility of the rare earth hydroxides. This sharp increase in the solubility may be due to the formation of more soluble double or/and complex salts.

These results however, suggest an interesting possibility of an initial rapid separation of (*a*) yttrium and erbium from (*b*) lanthanum and cerous solutions; and also the fractionation of (*b*) especially under conditions involving large amounts of the material.

Similar work on other rare earth hydroxides is in progress.

The authors are indebted to Professor S. S. Joshi for facilities, advice and kind interest in this work and to the National Institute of Sciences of India for award of a research fellowship to one of them (G.S.D.).

Summary

The behaviour of rare earth hydroxides towards variously concentrated solutions of sodium potassium tartrates is studied. Their solubility varies in the order $Ce^{iii} > La$; that of erbium, yttrium and ceric is, however, found to be almost negligible. This suggests a fairly rapid method of separation of rare earths (*a*) yttrium and erbium from (*b*) lanthanum and cerous salts; and the fractionation of (*b*).

References

1. Britton .. *J. Chem. Soc.*, 1926, 269.
2. ——, Battrick .. *Ibid.*, 1932, 196.
3. Mellor .. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, 1924, **5**, 570.
4. Thomson .. *Phil. Mag.*, 1811, **37**, 278.
5. Spencer .. *The Metals of the Rare Earths*, Longmans, Green & Co., 1919, p. 39.
6. Sen .. *J. Phys. Chem.*, 1925, **29**, 1533.

VISIBLE FLUORESCENCE AND CHEMICAL CONSTITUTION OF COMPOUNDS OF BENZO-PYRONE GROUP

Part IV. Further Study of γ-Pyrone Derivatives

V. V. SREERAMA MURTI, S. RAJAGOPALAN AND L. RAMACHANDRA ROW

(From the Departments of Chemistry, Andhra and Delhi Universities)

Received August 30, 1951

(Communicated by Prof. T. R. Seshadri, F.A.SC.)

IN the first part[1] of this series a general study of both the α and γ types of benzo-pyrones was made; in the subsequent two papers[2] the coumarins received detailed attention and attempts were made to explain the special features that were noted. As a result of synthetic work in our laboratories during the following years a large number of chromones, flavones, flavanones and isoflavones have become available. These have now been examined for their fluorescence in sulphuric acid solution and the results recorded here. Alkaline solutions were unsuitable because of the deep colour which these substances develop. For the observation of the fluorescence a pyrex test tube and diffuse light were employed and the light was concentrated by using a flat-bottomed round flask containing water. Brighter light such as direct sunlight passed through a similar condenser or reflected sunlight was not quite suitable because under these conditions even the pyrex tube started emitting a weak bluish-violet fluorescence. In those cases where the solution was deep yellow, brown or red it was diluted suitably with more sulphuric acid and the fluorescence observed. In all cases the intensity was checked after an hour; but no fading was noted in any case. The following table gives the list of compounds which show fluorescence:—

Compound	Colour of the solution	Fluorescence
Chromones		
7-OH-2-Me	Pale yellow	Bright violet
7-OMe-2-Me	do.	Strong bluish-violet
7-OH-3-OMe-2-Me	Colourless	do.
7-OAc-3-OMe-2-Me	do.	do.
7-Allyloxy-3-OMe-2-Me	do.	Blue
7-OH-8-allyl-3-OMe-2-Me	Pale yellow	Bluish-green
7-Allyloxy-8-allyl-3-OMe-2-Me	do.	do.
7: 3-Dimethoxy-2 : 8-dimethyl	Yellowish-brown	do.

Compound	Colour of the solution	Fluorescence
Flavones		
6-Hydroxy	Pale yellow	Blue
7 : 3′ : 4′-Trihydroxy	Pale red	Pale violet
7 : 3-Dihydroxy	Pale brown	Violet-blue
7 : 3 : 4′-Trihydroxy	Pale Yellow	Strong bluish-green
Robinetin	Orange	Strong green
5 : 7-Dihydroxy	Bright yellow	Blue
Apigenin	do.	Strong blue
3 : 5 : 7 : 4′-Tetrahydroxy	Brighter yellow	Intense blue
Quercetin	Brownish-yellow	Intense greenish-blue
Myricetin	Yellow	Bluish-green
Morin	do.	Strong greenish-blue
3 : 6 : 7-Trihydroxy	Pale yellow	Pale blue
3 : 6 : 7 : 4′-Tetrahydroxy	Almost colourless	Bright blue
3 : 6 : 7 : 3′ : 4′-Pentahydroxy	Yellow	Blue
3 : 6 : 7 : 3′ : 4′ : 5′-Hexahydroxy	do.	Bluish-green
Baicalein (natural)	Pale yellow	Pale blue
5 : 6 : 7 : 3′ : 4′-Pentahydroxy	Deep yellow	do.
Nor-tangeretin	Yellow	Blue
Gossypetin (natural)	Reddish-brown	Prominent blue
Hibiscetin (synthetic)	Brownish-yellow	Weak blue
3 : 7-Dihydroxy-4′-methoxy	Yellow	Bright blue
5-Hydroxy-7-methoxy	Bright yellow	Blue
5-Hydroxy-7 : 2′-dimethoxy	Pale yellow	do.
5 : 7-Dihydroxy-4′-methoxy	Bright yellow	Strong blue
5 : 7-Dihydroxy-3′ : 4′-dimethoxy	Brighter yellow	Blue
5-Hydroxy-7 : 3′ : 4′-trimethoxy	do.	do.
5 : 7-Dihydroxy-3′ : 4′ : 5′-trimethoxy	do.	do.
5 : 7-Dihydroxy-3-methoxy	Bright yellow	do.
5 : 7-Dihydroxy-3 : 4′-dimethoxy	Brighter yellow	Intense blue
Pentamethyl gossypetin (5-OH)	Bright yellow	Weak blue
7-Methoxy	Colourless	Strong blue
3 : 7 : 4′-Trimethoxy	Yellow	Greenish-blue
Pentamethyl robinetin	Bright yellow	Weak green
Kanugin	Deep red	Strong green
3 : 7 : 8 : 3′ : 4′-Pentamethoxy	Bright yellow	Weak blue
5 : 7 : 4′-Trimethoxy	Almost colourless	do.
3 : 5 : 7-Trimethoxy	Yellow	Bluish-green
3 : 6 : 7 : 3′ : 4′ : 5′-Hexamethoxy	do.	Weak bluish-green
Hexamethyl myricetin	Bright yellow	Green
3 : 5 : 7 : 8-Tetramethoxy	Yellow	Weak blue
Heptamethyl hibiscetin	Deep orange-yellow	Blue

Compound	Colour of the solution	Fluorescence
3:5:6:7-Tetramethoxy	Almost colourless	Feeble blue
Tangeretin	Deep yellow	Greenish-blue
3:5:6:8:4′-Pentamethoxy	do.	Blue
5:6:7:3′:4′-Pentamethoxy	Yellow	Light blue
5:6:7:8-Tetramethoxy	Pale yellow	do.
5:6:7:8:4′-Pentamethoxy	Yellow	do.
3:5:6:7:8-Pentamethoxy	do.	Weak blue
Dimethyl calycopterin	do.	Light blue
Isoflavones		
7-Hydroxy-2-Me	Light yellow	Bluish-violet
7-Methoxy-2-Me	Colourless	do.
7-Allyloxy-2-Me	Pale yellow	Dull blue
7-Hydroxy-8-allyl-2-Me	Colourless	Greenish-blue
7-Methoxy-8-allyl-2-Me	do.	Bluish-violet

The following compounds do not show any fluorescence on dissolution in concentrated sulphuric acid; the colour of the solution is given within brackets:—

**Chromones.*—7-Hydroxy-3-acetyl-2-methyl (pale yellow); 7-Methoxy-3-acetyl-2-methyl (very pale yellow); 7-Hydroxy-3-methoxy-8-aldehydo-2-methyl (yellow); 5:7-Dihydroxy-2-methyl (pale yellow); 5-Hydroxy-7-methoxy-2-methyl (colourless); 3:5:7-Trihydroxy-2-methyl (pale yellow); 5:7-Dihydroxy-3-methoxy-2-methyl (pale yellow); 5-Hydroxy-3:7-dimethoxy-2-methyl (pale yellow); 7:8-Dihydroxy-3-acetyl-2-methyl (yellow); 7:8-Diacetoxy-3-acetyl-2-methyl (yellow); 7:8-Dihydroxy-2-methyl (pale yellow); 7:8-Dimethoxy-2-methyl (colourless); 7:8-Dihydroxy-3-methoxy-2-methyl (pale yellow); 3:7:8-Trimethoxy-2-methyl (pale yellow); 3:5:7:8-Tetrahydroxy-2-methyl (orange-red); 3:5:7:8-Tetramethoxy-2-methyl (lemon yellow).

Flavones.—5-Hydroxy (red); 5-Methoxy (pale yellow); 3:5:4′-Trihydroxy (pale yellow); 3:5:3′:4′-Tetrahydroxy (yellowish-brown); 3:5:3′:4′-Tetramethoxy (pale red); Isokanugin (yellow); 6-Hydroxy-5-aldehydo (orange); 5:6-Dihydroxy (deep yellow); 5-Hydroxy-6-methoxy (bright yellow); 5:6-Dimethoxy (bright yellow); 3:5:6-Trihydroxy (yellow); 3:5:6:4′-Tetrahydroxy (yellow); 3:5:6:3′:4′-Pentahydroxy (yellow); 5:7-Dihydroxy-8-aldehydo (reddish-yellow); 5-Hydroxy-7:2′-dimethoxy (yellow); Primetin (brownish-yellow); 5-Hydroxy-8-methoxy (deep yellow);

* Some of these exhibit some fluorescence when their solutions in sulphuric acid are allowed to stand for over 24 hours.

3:6:7-Trimethoxy (almost colourless); 7:8-Dihydroxy (bright yellow); 3:7:8-Trihydroxy (yellow); 3:7:8-Trimethoxy (pale yellow); 3:7:8:4′-Tetramethoxy (deep yellow) 3:7:8:3′:4′-Pentahydroxy (yellow); 3:7:8:3′:4′:5′-Hexahydroxy (pale yellow); Nor-wogonin (yellow); Wogonin dimethyl ether (yellow); 5:7:8:2′-Tetramethoxy (yellow); Oroxylin-A (orange); 3:5:6:7:3′:4′:5′-Heptamethoxy (yellow); Pentamethyl herbacetin (deep yellow); 6:7:8:4′-Tetrahydroxy (pale yellow); 3:6:7:8:4′-Pentamethoxy (yellow); 5:6:7:8-Tetrahydroxy (orange); 5:6:7:8:3′:4′-Hexahydroxy (brownish-yellow); 3:5:6:7:8:3′:4′:5′-Octamethoxy (yellow).

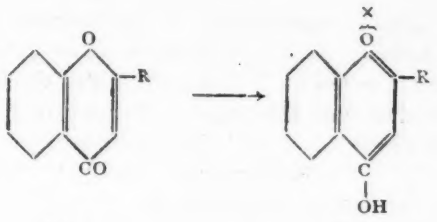
Flavanones.—7-Methoxy (bright yellow); 5:7-Dihydroxy (bright yellow); 5-Hydroxy-7-methoxy (bright yellow); 5:7:4′-Trihydroxy (bright yellow); 7-Methoxy-5:4′-dihydroxy (bright yellow); 5-Hydroxy-7:4′-dimethoxy (yellow); 5:7:3′:4′-Tetrahydroxy (orange-yellow).

Isoflavones.—7-Hydroxy-2-methyl-8-aldehydo (colourless); 7-Hydroxy-2-methyl-8-acetyl (colourless); 5:7-Dihydroxy (yellow); 5-Hydroxy-7-methoxy-(very pale yellow); 5:7-Dihydroxy-2-methyl (pale yellow); 5-Hydroxy-7-methoxy-2-methyl (pale yellow); 5:7-Dimethoxy-2-methyl (colourless); 7:8-Dihydroxy-2-methyl (pale yellow); 7:8-Dimethoxy-2-methyl (pale yellow); Prunetin (very pale yellow); Santal (pale greenish-yellow).

Discussion

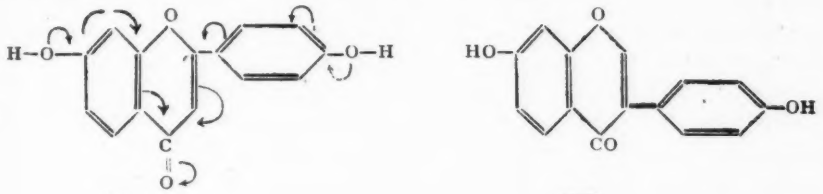
In the case of the chromone derivatives the relationship between fluorescence and chemical constitution seems almost parallel to that found in the coumarin field. Chromone itself has been reported to exhibit strong blue fluorescence in concentrated sulphuric acid whereas coumarin does not. A greater tendency to fluoresce seems to be exhibited by the chromone derivatives all through. This may be explained as due to the greater readiness with which the γ-pyrone structure (I) undergoes changes into the pyronium or hydroxy-pyrylium salts (II) which seem to be the real fluorescent substances in acid solution. The pyrone double bond is quite essential not only in the coumarins but also in the chromones. The flavanones which do not have this double bond are non-fluorescent.

The influence of the hydroxyl and methoxyl groups is most favourable to fluorescence in γ-pyrone derivatives when they are present in the 7-position and the 6-position is the next best whereas 5 and 8 positions are highly disadvantageous. The explanation offered earlier in regard to the behaviour of coumarins and pyrylium salts may be applicable to the present case also because they all refer to oxonium salts.[3] Formyl and acetyl groups reduce



(I) (II)

fluorescence while methyl has no appreciable effect. In the case of the coumarins it was pointed out that a phenyl group in the 3-position greatly enhances fluorescence whereas such a group in the 4-position has no advantage. Analogous features are noticed even in the chromones. A 2-phenyl derivative (flavone) is markedly more fluorescent whereas a 3-phenyl derivative (isoflavone) seems to be just the same as the corresponding chromone without the phenyl group. This difference could be attributed to the presence of conjugation between the C = O group and the phenyl group when present in the 2-position and its absence when the phenyl group is present in the 3-position (formulæ III and IV). Further it would appear that in regard to fluorescence in sulphuric acid solution conjugation of the hydroxyl group with the carbonyl group is a favourable feature and the electromerisations involved are given in the following formula. The importance of this feature is shown by the marked effect of a hydroxyl group in the 4′-position of the flavones (III) increasing the fluorescence considerably while in the isoflavone series (IV) no such influence is noticeable.



(III) (IV)

Our grateful thanks are due to Prof. T. R. Seshadri for his kind interest in this work.

References

1. Rangaswami and Seshadri .. *Proc. Ind. Acad. Sci.*, 1940, **12 A**, 375.
2. ———, ——— and Venkateswarlu .. *Ibid.*, 1941, **13 A**, 316.
   Balaiah, Seshadri and Venkateswarlu .. *Ibid.*, 1942, **16 A**, 68.
3. Row and Seshadri .. *Ibid.*, 1944, **19 A**, 141.

THE EFFECT OF WETTING AGENTS ON THE ADSORPTION OF CRYSTAL VIOLET BY GLASS*

By R. S. Subrahmanya, M. R. A. Rao and K. S. Gururaja Doss, F.A.Sc.

Received October 4, 1951

Introduction

The adsorption of wetting agents by wool under varying conditions of acidity has been extensively investigated by Neville and Jeanson.[1] They have also studied the influence of the wetting agents on the adsorption of dyestuffs by wool. McBain and co-workers[2] have studied the influence of salts and of soap on the adsorption of basic dyes by the walls of glass vessels. The following investigation was undertaken with a view to determine quantitatively the relative efficiencies of different wetting agents in their detergent action under a given set of conditions of acidity and concentration of crystal violet.

Experimental

Materials used

Glass powder.—Glass powder between 100 and 150 mesh was heated on a water-bath with 1 N hydrochloric acid for four hours and then washed free from chloride, and finally dried at 175° for one hour.

Crystal violet solution.—Khalbaum's C.P. crystal violet was employed. The purity of this chemical was tested by igniting a known amount in a platinum crucible and heating the resulting ash with a drop of concentrated sulphuric acid. The sulphate obtained by this method formed 5% of the weight of the solid taken for ignition. Since highly dilute solutions of this material were employed, the chemical was not purified further. To avoid the change in concentration of a standard solution, due to the adsorption of the dye by the glass walls of the measuring flask, the flask was shaken up with the solution of the dye till its surface was in equilibrium with the dye and the solution was thrown out. By repeating this process, a glass surface saturated with the dye was obtained. A fresh solution was then prepared in this measuring flask and kept as the stock solution of the dye.

Wetting agents.—1. *Aerosol O.T.*—The C.P. quality product was used without further purification.

* Part of the thesis submitted by Mr. R. S. Subrahmanya for the M.Sc. Degree of the Mysore University.

2. *Igepon T.*—The commercial sample was extracted with absolute alcohol and the wetting agent was recovered from the alcohol solution by distilling off the solvent.

Buffer solutions.—Acetate buffers were employed upto a pH of 6, phosphate buffer for pH 7·5 and sodium carbonate and sodium chloride mixture for pH 9·1. The quinhydrone electrode was used to determine the pH of acetate and phosphate buffers and the glass electrode for the sodium carbonate buffers.

Effect of pH on the adsorption of crystal violet by glass powder

1 c.c. of the buffer solution (0·2 M electrolyte concentration) was diluted to 9 c.c. with water and 1 c.c. of the stock solution of crystal violet was added to this and shaken well. 1 g. of the glass powder was then added and the mixture shaken on a shaking machine till equilibrium was attained. For each mixture, the time required for the attainment of equilibrium was determined separately. The concentration of the crystal violet in the equilibrium mixture was colorimetrically determined. It was noticed that a small quantity of crystal violet (about 1%) was invariably retained on the glass surface of the bottle used for shaking the mixture. In every experiment a correction was applied for the dye thus adsorbed, by dissolving out the dye with alcohol and estimating it. To the crystal violet solution employed as colour standard the buffer solution was added to have the same pH in the two solutions during colour comparison. The weights of the dye adsorbed at different pH values by one gram of the glass powder are given in Table I.

TABLE I

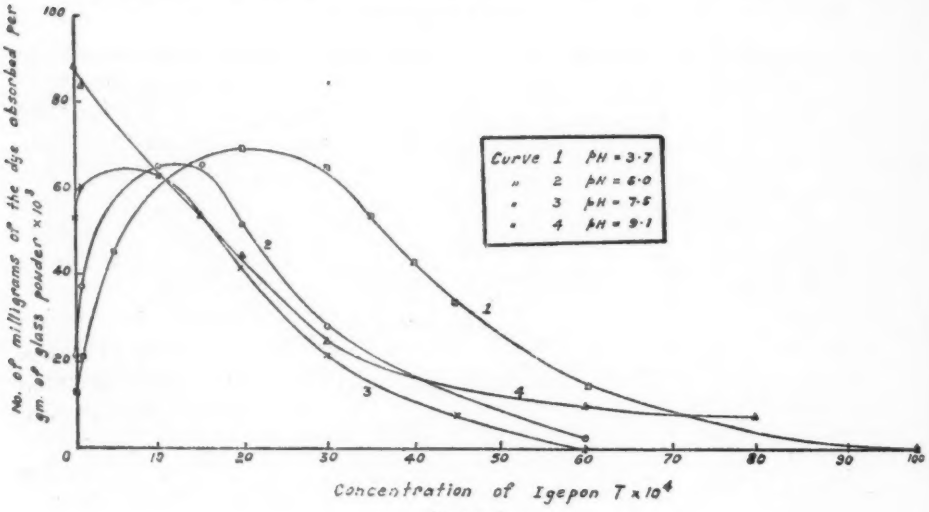
Effect of pH on the adsorption of crystal violet by glass

pH of the solution	No. of milligrams of the dye adsorbed per gram glass powder
3·7	0·013
6·0	0·021
7·5	0·054
9·1	0·089

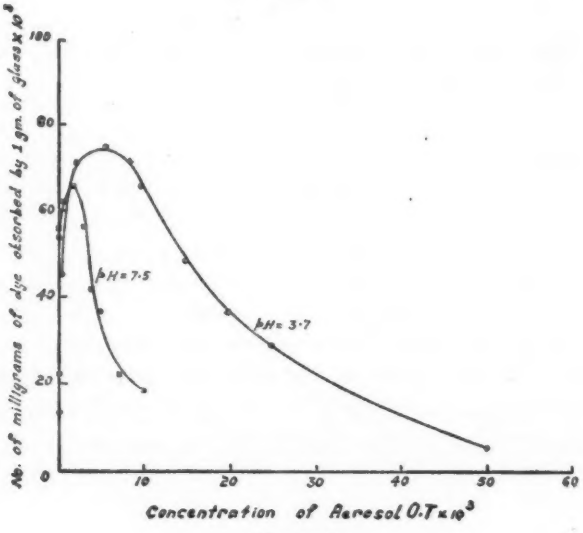
The influence of wetting agents on the adsorption of crystal violet

1 g. of the glass powder was added to 10 c.c. of the dye solution (prepared in the way indicated above) containing a known amount of the wetting

agent. After the attainment of equilibrium, the concentration of the crystal violet in the supernatant liquid was determined. As usual, the standard used for colour comparison had the same amount of the buffer and the wetting agent as the test solution. The experiment was repeated with different concentrations of the wetting agent. The quantities of the crystal violet adsorbed by 1 g. of the glass powder at various concentrations of Igepon T and Aerosol O.T. are given in Graphs I and II.


No. of milligrams of the dye absorbed per gm. of glass powder × 10³
Curve 1 pH = 3·7
" 2 pH = 6·0
" 3 pH = 7·5
" 4 pH = 9·1
Concentration of Igepon T × 10⁴

GRAPH 1



GRAPH 2

Discussion

1. *Effect of pH on the adsorption of crystal violet by glass.*—Table I shows that the amount of crystal violet cation adsorbed on glass increases with the pH of the solution. In the system studied the H^+ ion is the chief competitor to the dye cation for adsorption. At low pH values the H^+ ion almost completely replaces the dye molecule at the surface so that the adsorption of the dye becomes practically zero. As the pH increases the adsorption of the dye also progressively increases.

2. *Influence of Igepon T on the adsorption of crystal violet by glass at different pH values.*—Reference to Graph I shows that at pH values of 7·5 and below, the first addition of Igepon T increases the extent of adsorption of crystal violet on glass. On continued addition of the wetting agent, however, the amount of adsorption falls off and practically drops to zero at high concentrations of the wetting agent. The following explanation can be offered to account for this unexpected phenomenon. The polar groups of the dye are mainly responsible for the adsorption of the dye on glass since the hydrophobic portion of the dye may be expected to have no attraction to any atom or group present at the surface of glass. The amount of the dye adsorbed at equilibrium would depend on the density of charge on the adsorbed surface. A high charge density would by Coulomb repulsion diminish the life of the adsorbed dye ion at the surface. In the system studied, the Igepon T forms a complex by the union of the hydrophobic group with that of the dye ion. As the wetting agent is negatively charged, the average density of charge at the adsorbed surface would get diminished. The life of the adsorbed dye ions would thus get increased thereby increasing the adsorption by the addition of the wetting agent. It is also possible that at low pH values the increased adsorption of the positively charged dye may be due to increase in negative charge of the glass surface by the adsorption of the wetting agent.

At higher concentrations of the wetting agent, the decrease of adsorption of the dye is due to the wetting agent forming negatively charged complexes with the dye which are repelled by the negatively charged glass surface.

It is of interest to note that at higher pH values the wetting agent diminishes the adsorption of the dye considerably. The falling off, of adsorption of the cation begins at a concentration of 0·002% and 0·0006% of the wetting agent when the respective pH values are 3·7 and 7·5. At higher pH values the negative charge on the glass surface is considerably enhanced causing a diminution in adsorption of the negatively charged complex of the dye with the wetting agent.

3. *Influence of Aerosol O.T. on the adsorption of crystal violet by glass at different pH values.*—The adsorption curves for Aerosol O.T. at pH values 3·7 and 7·5 are plotted in Graph II. Experiments at pH 9·1 could not be tried owing to the hydrolysis of the wetting agent at this pH value. Curves obtained with Aerosol O.T. are similar in shape with those got with Igepon T and the same explanation holds good.

The technique of measuring the adsorption of crystal violet by glass, described above, gives us a method of comparing the detergent action of various wetting agents. At pH 3·7 for instance, 50% of the dye is adsorbed at a glass surface when the concentrations of Aerosol O.T. and Igepon T are 0·014% and 0·004% respectively. At this pH value therefore, Igepon T is nearly 3·5 times more powerful as a detergent than Aerosol O.T.

SUMMARY

1. The effect of pH and of wetting agents on the adsorption of crystal violet at the surface of glass has been investigated.

2. At low pH values, a wetting agent at first increases the adsorption of the dye. But with an increase in the concentration of the wetting agent the adsorption falls off rapidly and drops almost to zero. At higher pH values the wetting agent diminishes increased adsorption of the dye. An explanation has been offered to account for these observations.

REFERENCES

1. Neville and Jeanson .. *J. Phy. Chem.*, 1933, **37**, 1001.
2. McBain and Co-workers .. *Chem. Products*, 1941, **4**, 19.

EFFECT OF SALTS ON THE DETERMINATION OF pH BY THE INDICATOR METHOD IN PRESENCE OF IGEPON T*

By R. S. Subrahmanya, M. R. A. Rao and B. Sanjiva Rao, F.A.Sc.

Received October 3, 1951

While investigating the effect of Igepon T on the colorimetric method of determination of pH, it was noticed that the pH changed considerably when sodium chloride was added to the solution. A similar effect was also noticed when sodium sulphate and calcium chloride were employed, in place of sodium chloride. A systematic study of this interesting effect was undertaken.

Experimental

To remove the salt impurities in Igepon T, the solid was shaken up with ethyl alcohol and the clear solution was distilled off. The solid thus obtained had an ash content of 5·0%. 0·02% solutions of thymol blue and bromophenol blue were employed. In the following investigations, the concentrations of the indicator, the wetting agent and the buffer solutions were kept constant, while the concentration of the salt was changed.

Effect of sodium chloride on Igepon T-Thymol blue systems.—To 5 ml. of the acetate buffer (0·02 M) electrolyte concentration) 1 ml. of the thymol blue solution and 1 ml. of 0·5% of Igepon T solution were added and the total volume made up to 10 ml. The pH of this solution as determined by the glass electrode was 3·09. The pH was also determined colorimetrically employing Gillespie's method, using a Hellige Colorimeter. The acidic and basic standards of the indicator, employed for comparison, consisted of hydrochloric acid (0·2 N) and acetate buffer (4·7 pH) respectively, having the same concentrations of the indicator, the salt and the wetting agent as in the test solutions. The pH by the colorimetric method (apparent pH) was calculated by the equation

$$pH = pK + \log \frac{\text{basic form}}{\text{acidic form}},$$

where K is the dissociation constant of the indicator.

To another sample of the buffer-indicator-wetting agent mixture prepared as above, a known amount of sodium chloride was added and its

* Part of the thesis submitted by R. S. Subrahmanya for the M.Sc. Degree of the Mysore University.

apparent and true pH values were determined. The experiment was repeated for various concentrations of sodium chloride.

The effect of sodium sulphate and calcium chloride on the pH shift was also investigated.

Using bromophenol blue as the indicator, the pH shift was determined for varying concentrations of sodium and calcium chlorides. The following tables give the results obtained.

The shift in pH is expressed as:

$(-\Delta pH)$ = pH by the glass electrode − pH by the indicator method.

TABLE I

Igepon T-Thymol blue-Sodium chloride systems

pH of buffer = 3·09

Electrolyte concn. of buffer = 0·01 M

Molar concentration of sodium chloride	$-\Delta pH$
0·00	1·73
0·02	1·62
0·04	1·57
0·05	1·54
0·06	1·47
0·08	1·41
0·10	1·32
0·30	1·18
0·50	1·07
0·80	1·00
1·10	1·00

TABLE II

Igepon T-Thymol blue-Sodium sulphate system

pH of buffer = 3·09

Electrolyte concn. of buffer = 0·01 M

Molar concentration of sodium sulphate	$-\Delta pH$
0·00	1·73
0·01	1·68
0·02	1·59
0·03	1·51
0·04	1·47
0·05	1·42
0·40	1·05

TABLE III

Igepon T-Thymol blue-Calcium chloride system

pH of buffer = 3·09

Electrolyte concn. of buffer = 0·01 M

Molar concentration of calcium chloride	$-\Delta$pH
0·000	1·73
0·00016	1·63
0·00049	1·54
0·0008	1·44
0·0011	1·36
0·0015	1·26
0·0016	1·20
0·0033	1·15
0·0049	1·12
0·0065	1·11
0·0200	0·90
0·0330	0·80
0·0800	0·75

TABLE IV

Igepon T-Bromophenol blue-Sodium chloride system

pH of buffer = 4·27

Electrolyte concn. of buffer = 0·005 M

Molar concentration of sodium chloride	$-\Delta$pH
0·00	0·08
0·02	0·15
0·10	0·26
0·30	0·42
0·50	0·49
0·80	0·53

TABLE V

Igepon T-Bromophenol blue-Calcium chloride system

pH of buffer = 4·27

Electrolyte concn. of buffer = 0·005 M

Molar concentration of calcium chloride	$-\Delta$pH
0·0000	0·08
0·00017	0·11
0·00041	0·15
0·0017	0·23
0·0041	0·27
0·016	0·39
0·033	0·42
0·050	0·45

TABLE VI

Igepon T-Thymol blue-Calcium chloride system

pH of buffer = 3·08

Electrolyte concn. of buffer = 0·01 M

Concn. of Igepon T = 0·10%

Molar concentration of calcium chloride	$-\Delta$pH
0·0000	1·89
0·0016	1·40
0·0024	1·36
0·0049	1·25
0·0055	1·21
0·0065	1·10
0·0330	0·90
0·0800	0·80

DISCUSSION

1. *Effect of Sodium chloride on Thymol blue-Igepon T systems.*—Table I shows that the rate of fall of $-\Delta$ pH is rapid in the beginning but with an increase in concentration of the salt, $-\Delta$ pH attains a limiting value. This can be explained in the following manner. Thymol blue is uncharged[2] in the acid form and has a single negative charge, in the basic form. At a given pH of the buffer, there will be an equilibrium between the acid and the basic forms, governed by the equation

$$pH = pK + \log \text{basic form} / \text{acidic form} .$$

When the wetting agent is added, a complex is formed between the wetting agent and the indicator. The stability of this complex however, depends upon the nature of the ions produced by the wetting agent and the indicator. In the case of thymol blue system, the extent of complex formation between the negatively charged basic form of the indicator and the anion of the wetting agent, will be comparatively small, owing to the like charges. On the other hand, a complex of higher stability is formed between the acid form of the indicator, which is uncharged, and the anion of the wetting agent. Formation of this complex shifts the equilibrium between the acidic and the basic forms of the indicator. As the complex has the same colour effect as the free acid form of the indicator, there is an apparent enhancement of the acid form and the pH of the solution appears as having shifted to the acid side. A salt added to the system scarcely affects the formation of the complex between the uncharged acid form of the indicator and the anion of the wetting agent.[1] But, as the salt lowers the zeta potential, it reduces

the repulsion between the anions of the wetting agent and of the basic form of the indicator and enhances the tendency to form a complex between the two (*viz.*, wetting agent and the basic form of the indicator). The shift in pH thus becomes less. It is known that the zeta potential is reduced to a limiting value with the progressive addition of a salt.[3] The formation of the complex between the wetting agent and the basic form of the indicator and consequently the value of $-\Delta$ pH can therefore be expected to reach a limiting value.

2. *Effect of Sodium sulphate on Thymol blue-Igepon T systems.*—The results obtained with sodium sulphate are similar to those got with sodium chloride. This is to be expected, as we are dealing with the same cation, in the two salts.

3. *Effect of Calcium chloride on Thymol blue-Igepon T systems.*—In general, calcium chloride affects the system in the same way. But the effect of concentration of salt is far more marked than in the case of sodium chloride. This is due to the divalency of the cation of the salt. The ratio of the concentrations of sodium and calcium ions required to induce the same pH shift, is about 40, as in the case of the " Hardy-Schulze Law ".

The effect of aluminium chloride could not be tried as the wetting agent was precipitated by this salt. The results in Tables III and VI indicate that the general nature of the pH shift remains practically unaltered when the concentration of the wetting agent is changed from 0·05% to 0·1%.

4. *Effect of Sodium chloride on Bromophenol blue-Igepon systems.*—In this system, the shift in pH, *viz.*, $-\Delta$ pH increases with an increase in the concentration of the salt. This effect is the opposite of what has been noticed in the case of Thymol blue-Igepon T systems but can be explained on the same basis, *viz.*, the influence of the electrical charge on complex formation. Unlike thymol blue, the indicator bromophenol blue has one negative charge in the acid form and two negative charges in the basic form. The repulsion between the acid form of the indicator and the wetting agent ion is therefore much lower than that between its basic form and the wetting agent. Complex formation between the acid form of the indicator and the wetting agent will be greater than that between the basic form and the wetting agent. The apparent pH will therefore be always lower than the pH got by E.M.F. method. When a salt is added, the zeta potential will be lowered in both forms of the indicator. But the effect of the negative charge on the basic form would be roughly twice as great as on the acid form of the indicator. Complex formation with the basic form will therefore be less. Owing to the relatively larger formation of the complex of the acid form

the value of $-\Delta$ pH increases with an increase in the concentration of the salt.

The results obtained with calcium chloride are similar in nature to those got with sodium chloride. As pointed out already, the effect of concentration on the change of $-\Delta$ pH is very pronounced. The reasons for such a behaviour have already been discussed.

Summary

1. In presence of Igepon T, the pH of solutions, as measured colorimetrically with thymol blue and bromophenol blue as indicators, is found to be lower in value than that obtained with the glass electrode. The value of $-\Delta$ pH (pH by the glass electrode $-$pH by the colorimetric method) is found to be influenced by the presence of salts like sodium chloride, sodium sulphate and calcium chloride.

2. With thymol blue, an increase in salt concentration diminishes the value of $-\Delta$ pH, while with bromophenol blue the opposite effect is observed.

3. With calcium chloride, the effect of salt concentration on $-\Delta$ pH is far more pronounced than with sodium chloride.

4. The results are explained on the basis of the effect of the salts on zeta potential, in relation to the formation of complexes by the acidic and the basic forms of the indicator, with the wetting agent.

References

1. Krishnappa, Doss and Sanjiva Rao .. *Proc. Ind. Acad. Sci.*, 1946, **23 A**, 47.
2. Hartley .. *Trans. Far. Soc.*, 1934, **30**, 444.
3. Ham and Dean .. *Ibid.*, 1940, **36**, 52.

998-51—Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao Superintendent, and Published by The Indian Academy of Sciences, Bangalore